



DEGREE PROJECT IN ENERGY AND ENVIRONMENT,
SECOND CYCLE, 30 CREDITS
STOCKHOLM, SWEDEN 2019

Carbon Stability of Biochar

Methods for assessment and indication

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Carbon Stability of Biochar. Methods for assessment and indication.

Kolstabilitet i biokol. Metoder för värdering och indikation.

Keywords: Biochar, Stability, MRT, Carbon sink, Carbon stability, Negative emissions technology (NET)

Degree Project in Industrial Ecology, Second Cycle AL227X

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Acknowledgements

I am happy and proud to contribute to the fight against climate change! A proper prediction and estimation of the carbon sink that biochar entail is important to make the most efficient priorities for the climate and a sustainable future. I am grateful for the trust KTH and Stockholm Exergi gave me to conduct this study. I want to direct a special thanks to Kåre Gustafsson, Cecilia Sundberg and Elias Azzi that have support me with valuable knowledge, patience and commitment. Your contributions are invaluable! My family, husband and children, you are my motivation to work for a better future. You make it all possible!

Helena Söderqvist

Abstract

Biochar can reduce the amount of CO₂ in the atmosphere and is acknowledged as one feasible technology for negative carbon emissions. The stability of carbon in biochar is of major importance for the carbon sequestration value. A method for confident estimation of the stability is needed to make efficient priorities for the climate. The aim of this study is to identify the best available method that can be used to indicate the stability and quantify the carbon sequestration potential of biochar. The result builds on a literature review of the current state of scientific knowledge and the proposed method is tested with data from previous studies and then applied to the case of Stockholm Exergi.

Biochar has a stable carbon structure, always more recalcitrant than the biomass that it derives from. However, estimations of how stable the carbon are varying a lot in the literature. Biochar is not unambiguously defined, there is rather a range of materials with different stability and the degradation is context dependent. Further discrepancy in the estimated stability derives from different experimental design and approaches to modeling the data. There is a challenge to do a proper estimation of the actual degradation, due to the long time perspective and the complexity of observation of behavior in a natural system.

A functional method to indicate the stability of carbon in biochar is needed because a biochar producer cannot conduct a long term trial to prove the carbon sequestration potential. Several methods have in theory the ability to indicate stability. However, the H/C_{org} model with the expression BC₊₁₀₀ emerging to be the best suited method due to its connection to measured degradation, accessibility and acceptance. The H/C_{org} model could be further improved by calibration and validation by collecting existing data from previous assessments. Communication of the carbon sequestration after hundred years compared to other carbon sinks should be improved to better reflect the long term carbon sequestration value of biochar.

Stockholm Exergi is planning for a biochar production of 5 000 ton/year. The H/C_{org} method estimate that this corresponds to 9 000 – 11 500 ton CO₂ per year, stable for at least hundred years. The wide range in the result derives from the different interpretations on the H/C_{org} method, where the different interpretations derive from the variation that previous research result shows. This is an incentive to support further development of the method. The sequestered carbon in biochar must be protected in its application to ensure the carbon sink in a trade system. Biochar in soil, green areas and concrete face the risk of being dis/re-located. However, that is not a threat to the carbon sequestration value. Biochar and biochar in a soil product sold in bags cannot account for the biochar sequestration value detached from the product, because of the risk of incineration.

The future development of biochar stability assessment should in a short term assemble the existing knowledge of conducted trials and use that with knowledge of what approaches that best corresponds to the real stability of biochar. This could decrease the observed variations in the stability assessments and be used to calibrate and validate methods that could indicate stability. In the long perspective field trials and incubation trials should be done in a standardized way to assess the degradation, designed according to best practice with long trial times and consciously extrapolated data.

Sammanfattning

Biokol kan minska halten av CO₂ i atmosfären och är identifierad som en möjlig teknologi för negativa CO₂ utsläpp. Biokolets stabilitet har stor betydelse för dess potential. Målet med denna studie är att identifiera den bästa tillgängliga metoden för att indikera kolets stabilitet. Resultatet bygger på en litteraturgenomgång av befintligt kunskapsläge. Den föreslagna metoden testas med biokolsdata ifrån tidigare gjorda mätningar. Kolinbindningspotentialen i Stockholm Exergi's biokolsprojekt beräknas genom att applicera metoden på förväntad biokolsproduktion.

Biokol har en stabil kolstruktur, alltid mer stabil än den biomassa den härstammar ifrån. Uppskattningar av hur stabilt biokol är varierar mycket i litteraturen. Biokol är inte entydigt definierat utan är ett spann av olika material och dessutom är stabiliteten kontextberoende. Ytterligare variationer härstammar ifrån varierande experimentdesign och olika metoder som används för extrapolation av mätdata. För att beräkna kolinbinding i biokol som produceras behövs en metod som kan visa hur stabilt kolet är. Mätmetoden är resurskrävande och därför behövs istället ett samband mellan kolets innehåll/struktur och uppvisad stabilitet som kan användas i kombination med en enklare analys av det producerade biokolet för att indikera stabilitet. I teorin finns det många metoder som kan vara funktionella men enligt denna studie är H/C_{org} metoden i kombination med BC₊₁₀₀ index mest lämpligt att använda på grund av metodens uppvisade koppling till uppmätt stabilitet, tillgänglighet och acceptans.

Stockholm Exergi planerar för en biokolsproduktion på 5000 ton/år och H/C_{org} metoden uppskattar att detta årligen motsvarar 9 000 – 11 500 ton CO₂ stabilt i minst 100 år. Spannet som resultatet uppvisar beror av den variation av uppskattad stabilitet i litteraturen och är ett incitament för att stödja en vidare utveckling av metoden. I applikationen av biokol måste kolsänkan skyddas för att kunna ingå i ett handelssystem. För biokol till jordförbättring, grönområden i staden samt biokol i betong föreligger en möjlighet att biokolet blir omflyttat eller förloras ifrån den ursprungliga applikationen, detta medför dock inte att kolsänkan går förlorad och är därför inte ett problem för värdet av kolsänkan. Däremot bör värdet av kolsänkan av biokol som säljs i konsumentförpackningar inte frikopplas ifrån biokolsprodukten eftersom det då saknas kontroll över att kolet inte bränns.

Vidare studier av stabilitet av biokol bör på kort sikt innefatta insamling av befintlig data ifrån genomförda försök. Genom kunskap om hur olika faktorer inverkar på verklig och uppskattad stabilitet kan spannet av variation bättre accepteras och minska. Vidare kan insamlad data användas för att kalibrera och validera indikationsmetoder. Kommunikationen av kolsänkan av biokol och det långsiktiga värde som skiljer biokol ifrån andra mer kortsiktiga kolsänkor bör förbättras. Långsiktiga fält och inkubationsförsök bör etableras enligt kunskap om experimentell design och hantering av data för att på ett så korrekt sätt som möjligt spegla verklig stabilitet och kolsänka.

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1 Introduction

Biochar as a climate mitigation tool has large potential (Leng et al., 2019) and has recently been identified as a promising negative emission technology by the International Panel on Climate Change (IPCC, 2018). In the Special Report Global Warming of 1.5°C (SR1.5) biochar is described as one of the relevant mitigation options and there is robust evidence and high agreement that soil carbon sequestration and biochar is a feasible CO₂ removal method. The climate mitigation potential of biochar relies on the carbon stability, which make methods to accurately indicate the biochar stability highly interesting (Leng et al., 2019).

The energy utility Stockholm Exergi (SE) is owned by the Fortum corporation and the City of Stockholm. Currently, SE investigate how biochar can support a sustainable development and their vision of Stockholm as a carbon sink (Gustafsson, 2019). Stockholm Exergi has together with KTH (Sundberg, 2019) identified the need of a better overview of the knowledge of the carbon stability of biochar. A confident estimation of the carbon stability enables a quantification of the carbon sequestration potential of biochar. Such a quantification could support climate policy aimed at biochar as a climate mitigation tool. Furthermore, it would provide biochar producers and developers of biochar production techniques with confidence in their business strategy and security in investments (Gustafsson, 2019).

1.1 What is biochar?

Biochar is the solid product from pyrolysis of biomass in the absence of, or with limited access to oxygen. Biochar can share properties with charcoal but is intend to be used as a tool for environmental management such as soil improvement or carbon sequestration. Furthermore, biochar can, in contrast to charcoal, be produced from a wide range of different organic feedstocks (Lehmann & Joseph, 2009).

Biochar found in the black soil in the Amazon basin, called terra preta is one early sign of deliberate use of biochar as a soil amendment (Lehmann et al., 2006). Biochar found in that area has been dated to be 700 – 7000 years old (Lehmann & Joseph, 2009). The early use of biochar in a Swedish context is indicated by the notes of Carl von Linné, on how farmers mixed char coal with urine from cows and used it on the fields (Linné, 1734).

1.2 Biochar in a modern context

Biochar has the ability to sequester carbon. Moreover, the material properties of biochar have the potential to improve the resilience of resource restricted agricultural systems by improving the fertility and soil health (Quambrani et al., 2017). The structure of the biochar can be compared to a rigid sponge, where a large active surface and many different pore sizes can facilitate a better nutrient and water holding capacity (Lehmann & Joseph, 2009; Quambrani et al., 2017).

These material properties make biochar highly relevant to both climate change mitigation and adaptation. Furthermore, a biochar production system can contribute to several co-benefits, suitable for more circular solutions. Lehmann and Joseph (2009) distinguish four main benefits from a biochar production system. Besides carbon sequestration and soil amendment they mention energy production and waste management as added values.

Since biochar can be produced from different organic feedstocks it is possible to make biochar production a part of a waste management system, thus utilizing existing organic waste streams (Quambrani et al., 2017). The biochar production process reduces weight, volume and the risk of leakage of methane gases and nutrients (e.g. pyrolysis of manure) and could facilitate a better waste management

(Lehmann & Joseph, 2009). Material flows that are redirected from incineration to pyrolysis would move upwards in the waste hierarchy, since some of the energy recycling is displaced with material recycling (Anderson, 2018). However, the pyrolysis process generates excess heat that can be utilized in a district heating system or in heat demanding processes.

The biochar as a product has predominantly been used as a soil amendment due to the expected effects from the nutrient and water holding capacity (Lehmann & Joseph, 2009). There are, however, other possible uses for biochar as described by Anderson (2018) in a market feasibility study made in a Swedish context. Applications specifically identified by Anderson are: as a filler material in concrete; as a filter material; as a supplement to animal feed.

1.3 Biochar and carbon sequestration

The pyrolysis process reforms the fast degradable carbon compounds in the biomass into more stable structures in the biochar. These carbon structures are more resistant to degradation than the original carbon compounds in the biomass. In this way the amount of carbon in the atmosphere circulating in the fast cycle can be reduced when carbon is introduced into a slower carbon cycle (Lehmann & Joseph, 2009). This can be seen as a contrast to burning fossil fuels, that release carbon from the long term storage into the atmosphere (Quambrani et al., 2017).

There is a large variation of stated carbon stability of biochar in the literature. Reviews and meta studies of carbon stability shows a range from decades to millennium (Budai et al 2013; Lehmann & Joseph, 2015; Wang et al., 2016). Biochar has previously been regarded as recalcitrant to chemical and biological degradation (Cross and Sohi, 2011). That perception is supported by the findings of very old carbon in the same layer of soil as carbon with a more recent origin (Zimmermann and Gao, 2013). Contradictory to this conclusion, if biochar would be resistant to chemical and biological degradation all organic matter in soil would consist of biochar as a consequence of natural fires (Zimmerman, 2010). In addition, there are many recent studies that show that the carbon does degrade (Wang et al., 2016). Furthermore, Zimmerman and Gao (2013) point out that this contradiction with both degradable carbon and very old carbon co-existing is a result of biochar being a spectrum of different carbon compounds with different recalcitrance to degradation.

The stability of carbon in biochar thus has a central role for the sequestration potential and is therefore important to estimate (Leng et al., 2018). This is, however, a challenge due to several reasons. First of all, biochar is not an unambiguously defined material with specific characteristics, but rather a range of materials with different physical and chemical structures, originating from different production processes and a variety of feedstocks (Spokas, 2010). Secondly the stability of carbon, meaning for how long it will remain out of the faster carbon cycle, is context dependent since different applications will induce different levels of biotic and abiotic stress to the carbon (Wang et al., 2016). This variation in both biochar and its possible applications poses a challenge to finding a standardized method for predicting biochar stability.

Furthermore, the relevant time perspective is a challenge when evaluating and predicting the stability. To truly measure the degradation rate it would be necessary to monitor the degradation of carbon for hundreds of years or more. In practice this is not an option. Therefore, a more viable possibility is to mimic the natural degradation by simulating and modeling the degradation of biochar to estimate the stability (Leng et al., 2018). Such modeling is also a resource and time demanding process and it is reasonable to assume that it cannot be done by every biochar producer and for every batch of biochar. Therefor a reliable and more assessable method to indicate the stability is needed to connect a biochar property to a modelled degradation behavior in order to more easily estimate the carbon sequestration potential.

1.4 Aim and research questions

The aim is to identify the best available method to indicate and communicate the stability and carbon sequestration potential of biochar. The proposed method should then be used to estimate the carbon sequestration potential of Stockholm Exergis biochar project. Furthermore, potential risks for the carbon sequestration potential in the biochar application should be identified.

To achieve this, two questions will be answered:

- What is the best available method to indicate and quantify carbon sequestration potential, suitable for biochar production in the context of climate mitigation?
- What carbon sequestration potential can be expected from Stockholm Exergi biochar project?

The first question answering what method that is comprehensive enough to be scientific valid and accepted, but still manageable with respect to resources of time and costs. The second question is using the proposed method, but also contribute to define and delimit the scope of the first question. Using the case of Stockholm Exergi and their planned pyrolysis unit as an example, more applicable requirements can be suggested by addressing the intended raw materials and applications.

1.5 Objectives

- Review the current scientific state of knowledge of carbon stability of biochar and the knowledge on how to evaluate it and identify challenges and knowledge gaps.
- Identify methods theoretically viable for indicate carbon stability of biochar.
- Identify the best available method for the given context and propose how to use and develop it.
- Identify relevant requirements to protect the carbon sequestration value in the biochar application.
- Use proposed method to estimate confident carbon sequestration for SE.

1.6 Delimitations

The scope of this work is focusing on the stability of carbon in biochar. An overview of biochar is given to give context to the climate potential and the challenges to predict the climate benefits and the carbon sequestration but it is not claimed to give comprehensive knowledge of biochar in its application. Many aspects on the production and quality of the biochar regarding its environmental effects are important but not connected to the actual stability of biochar and had to be excluded from the scope. This study addresses the stability of carbon and the carbon sequestration potential but does not cover the total effect on the carbon balance of producing and using biochar.

2 Method

An initial literature study was conducted on the general state of knowledge of biochar in the context of climate mitigation. The focus was narrowed down in line with the purpose of this study to review the specific knowledge of stability of carbon of biochar and methods for measuring, modeling and indicate the stability of carbon in biochar. Articles and papers were found by using search words such as: biochar, stability, recalcitrant, mean residents time, biochar and climate. Biochar researchers at KTH have contributed to finding relevant articles. Some review articles have been particular important to this work

(Leng et al., 2018; 2019; Weber and Quicker, 2018; Wang et al., 2016). To evaluate the long term fate of biochar in different applications waste management organizations were contacted and the possible impact of each application was the foundation to the requirements that was later applied to the estimated carbon sequestration potential of Stockholm Exergi biochar project.

To illustrate the relative change of elemental composition in relation to highest treatment temperature diagram was constructed. Data was extracted graphically with an online tool (<https://apps.automeris.io/wpd/>) and the content of nitrogen was excluded due to low levels and the graphical method to extract data. The graphic illustration of the differences of pool- models was done to illustrate the difference of estimated stability. It was done in excel with a data series with origin in the mean degradation rates described by Wang et al. (2016) and the use of 1-pool model and 2-pool model.

All found methods that could have potential to indicate stability were reviewed. The methods to indicate and predict stability that were found during the literature study were then evaluated according to relevant criteria for the purpose of being a viable, robust and functional method to use for biochar producers to predict and estimate carbon stability. The first criterion, *Does the method have potential to provide an accurate result for the relevant range of carbon structures?* evaluated if the method could be a relevant method and a constrain for further evaluation of the method. The following criteria: *Available for biochar producers in terms of time and cost?* assessed if the method is or easily could become an available option for producers of biochar. The next criteria: *Is there a relation with measured MRT well declared?* refer to the connection in time, where the mean resident time (MRT) denominate the mean time that the carbon particle remains stable in the ground. If another time indicator was used was it noted. The last two criteria referred to the validity and acceptance of the methods.

The listed methods for indication of carbon stability in biochar were divided into three categories to according to their level of viability and the best suited method was then further investigated. This induced an interest to test the method's accuracy by comparing the result of other known MRT and elemental results from literature and a small scale test was conducted. Data from previously conducted stability assessments that included published data of the H/C ratio was found through a list of summarized research trials made by Lehmann and Joseph (2015). Further explanation, calculations and references can be found in appendix 1.

The carbon sequestration potential of Stockholm Exergi's biochar project was calculated from masses and type of feedstock, estimated biochar yield provided by Stockholm Exergi (Gustafsson, 2019). The calculations were done with values from an elemental analysis conducted by Eurofins (13/10 2017) on biochar produced from garden waste at Högdalen and for horse manure values for dairy manure were used, described by Lehmann & Joseph (2015). The sequestered carbon where calculated with different BC₊₁₀₀ stability (70 %, 80 % and 90 %) where 70 % represent the conservative value used by IBI and the 90 % (for the H/C_{org} 0.28) corresponds to the mean value if the H/C < 0.4 is assumed to have a linear trend. The CO₂ was calculated: $CO_2 = C \times 44 / 12$ as described by Shackley et al. (2016).

3 Result of literature review

This section gives an overview of the current state of knowledge of the carbon stability of biochar and how to evaluate and predict it. The aim is to give fundamental understanding of carbon stability and its importance for climate mitigation, what factors that affect the carbon stability and how stable biochar has shown to be. Last in the section the available methods that can be used to indicate stability of carbon are identified.

3.1 Biochar and its contribution to climate mitigation

The climate mitigating potential of biochar production requires the inclusion of the carbon sequestration and the indirect effects on the global carbon balance as a consequence of biochar production and application (Woelf et al., 2009). To truly evaluate the total effect a life cycle perspective is needed. Both effects that increase and decrease the actual effect on the carbon balance should be considered. There are many potential effects of biochar production and indirect effect on the surrounding system such as: avoided greenhouse gases emissions from soil; a more resource efficient nutrient management; improved agronomic efficiency; avoidance of emissions from traditional use of the biomass and the replacement of fossil fuels (Lehmann & Joseph, 2009).

In this study the carbon sequestration potential of biochar is of main interest. The potential depends on the content of carbon and how recalcitrant the carbon compounds are to abiotic and biotic degradation. The carbon sequestration potential is context dependent and will be affected of what biotic and abiotic stress the biochar exposed to in its application (Wang et al., 2016). Indirect effects on the carbon balance that come from the biochar application regarding soil organic matter, called priming effect, and enhanced net production of biomass which will also be briefly overviewed in the subsection.

3.1.1 Indirect effects on the terrestrial carbon balance

Biochar-induced priming refers to the effect the application of biochar has on the existing soil organic matter (SOM). By adding biochar negative priming could occur and the degradation of SOM decrease. However, the degradation could also increase as in positive priming, and thereby reducing the climate potential of biochar management (Fang et al., 2015). The carbon flux from an area sometimes increases when adding biochar to the soil. However, measuring the total flux of CO₂ means that the origin of carbon is not distinguished and the increasing amount in general derives from the small part of labile bioavailable compounds in the biochar (Cross and Sohi, 2011). Both positive and negative priming occur and can co-exist; the actual mechanisms behind it are still poorly understood. Wang et al. (2016) exemplifies some possible mechanisms: the negative priming could be explained with ideas that the easily available compounds in the added biochar are preferred over SOM or that biochar sorbs some of the flux from the soil. Another possible explanation could be a decrease of biological activity due to some additional content in the biochar. Positive priming could be explained by increased biological activity when biochar is added to sandy low fertility soils. Zimmerman et al. (2011) found that biochar produced at a higher temperature (525°C - 650°C) in general contributed to negative priming more often compared to biochar produced at a lower temperature.

Cross and Sohi (2011) conducted a test where isotopic methods were used to distinguish the origin of carbon flux from biochar amended soil. The test showed that biochar not induced any positive priming. Wang et al. (2016) made a meta-analysis that included 116 observations from 21 studies using methods to separate the SOM and the biochar flux of carbon dioxide. The analysis showed that even if there is a possible risk for positive priming in some low fertile sandy soils, the combined result from the meta-analysis clearly shows that biochar addition contributes to a negative priming that will last for several years after the biochar application (Wang et al., 2016).

Another indirect effect of biochar application that has the possibility to further impact the climate potential is the increasing amount of biomass that is expected with increased fertility and soil health (Lehmann et al., 2006). Wang et al (2016) states that the improved soil structure, the root growth and distribution, could increase the natural carbon bound in the soil. For instance, there have been observations in Kenya where biochar application to the field has more than doubled the production (Gitau et al., 2019) and a threefold increase of the yield was found on sandy soil (Kammann, et al., 2015). However, these results are context dependent and a corresponding result has not been shown in the context of Nordic climate and more fertile soils. The impact from indirect effects of biochar application are in the lifecycle perspective of climate mitigating potential important. In general, those indirect effects are adding values to the climate mitigation potential (Wang et al., 2016).

3.1.2 The effect of carbon stability on the level of carbon dioxide in the atmosphere

IPCC (2018) includes biochar as one of the carbon negative emission techniques that could be developed in order to balance the carbon budget to a sustainable level. The use of different negative emission techniques is sometimes associated with a leakage of carbon dioxide back to the atmosphere. The implications of that leakage has been studied by Lyngfelt et al. (2018). The degradation rate of carbon in biochar corresponds directly to that leakage of carbon dioxide and therefore, the result of this study is interesting in the context of discussing carbon stability. Lyngfelt et al., (2018) aims to answer the question if carbon storage just is transferring the problem to the future. They conclude that unless the leakage of carbon dioxide was rapid and substantial, the climate benefits of carbon capturing techniques would exceed the lost potential of leaking carbon dioxide. The mix of different degradation rates, as in different storages techniques, is beneficial to keeping the level of carbon dioxide down. In fact, the mix of three different degradation rates 300, 1 000 and 10 000 years was modeled for 800 Gt captured carbon and even with the assumption that it all leached out, the peak of carbon dioxide in the atmosphere was reduced by 75 %. The absolute numbers cannot be transferred to biochar, but the model by Lyngfelt et al. (2018) shows that the continuum of different degradation rates that constitute the biochar degradation behavior might be a strength in the climate mitigation context, even though it makes the prediction of the degradation more complicated.

3.2 What is affecting the carbon stability in biochar?

Two factors determine how long the carbon remains stable in the biochar: first the biochar properties meaning how recalcitrant the carbon compounds in the biochar are to biotic and abiotic degradation and secondly the stress from the environment that the carbon is exposed to in soil or other application (Mašek et al., 2013; Leng et al., 2019)

3.2.1 Physical and chemical composition of the biochar

The content and the composition of the biochar depends on the initial feedstock and what carbon compounds that are formed during the pyrolysis process. Woody feedstocks generates in general a more stable biochar with higher amount of carbon than biochar made from crop and grass (Wang et al., 2016). The ash in the feedstock remains in the biochar, and large variation between feedstocks can occur (Weber and Quicker, 2018). Klasson (2017) illustrated the transformation through the pyrolysis process using proximate analysis parameters of ash, volatile matter (VM) and fixed carbon (FC) (see Figure 1).

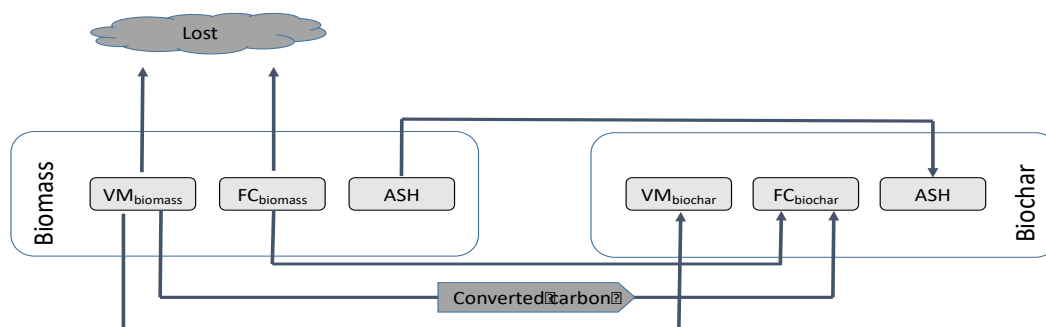


Figure 1. Simplified model for the transformation of biomass to biochar in the pyrolysis process based on proximate analysis, adapted from Klasson (2017).

An important production parameter for the biochar is the highest treatment temperature in the pyrolysis process (HTT). Weber and Quicker (2018) collected data on HTT and elemental analysis from different biochar. The development of relative weight distribution of atomic content (dry, ash free biochar) in relation to HTT can be seen in Figure 2. There is a clear relationship between the HTT in the process and the loss of functional groups and volatiles and where the main changes in the process occurred in the temperature range 200 – 400°C. The graph in Figure 2 considers the relative relationship between the carbon, oxygen and hydrogen, which is relevant for the prediction of what kind of compounds that constitute the biochar. The biomass will achieve a higher amount of aromatic carbon compounds and less functional groups and labile compounds with a higher treatment temperature (Wang et al., 2016). However, the absolute amount of carbon yield is decreasing with temperature because carbon in labile compounds will oxidize in the process and the ash content in relation to the biochar will also increase with temperature (Weber and Quicker, 2018).

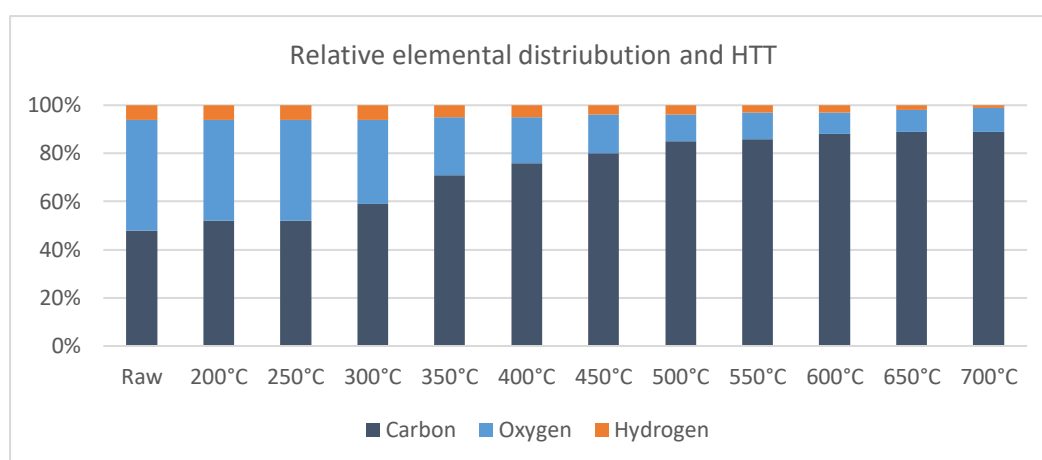


Figure 2. The relative weight distribution of carbon, oxygen and hydrogen in ash free dry biochar from woody feedstocks produced at different temperatures. Data adapted from Weber and Quicker (2018) nitrogen excluded.

The degradation behavior of a biochar and the total stability is a result of a spectrum of many individual different behaviors of carbon compounds (Zimmerman, 2010). Depending on the molar ratio of H/C and O/C the carbon is expected to be more or less aromatic/carbonized and therefore less reactive and more recalcitrant to degradation. In modeling compounds with similar degradation behavior are pooled together and commonly divided in a labile pool and a stabile pool (see section 3.5). In mean the labile pool of carbon is approximately 3 % of the total carbon and will have a minor effect of the overall sequestration potential of the biochar (Wang et al., 2016). The relative distribution of carbon, hydrogen and oxygen in the biochar indicates the degree of carbonization/aromaticity since the more aromatic carbon ring structures contain less hydrogen and oxygen. At temperatures above 400 – 500°C aromatization and loss of functional groups contribute to forming larger complex of aromatic rings, likely to be very recalcitrant to both biotic and abiotic degradation (Zimmerman and Gao, 2013). Wang et al. (2016) gathered 24 studies and 128 observations and found a clear connection between the measured degradation rate of carbon and the HTT temperature.

The particle size of the feedstock can also contribute to the stability because the smaller particle will have a larger exposed surface to the ambient in the process relative to the amount of biochar. Manyà et al. (2014) studied the three main parameters for carbon sequestration in pyrolysis, HTT, particle size and the absolute pressure. It was found that the pressure had an impact on the secondary reaction where some of the released carbon compounds reform to a more stable structure. However, that effect could also be achieved by a longer residence time e.g. slow pyrolysis.

Another relevant thing for the estimation of stabile compounds is to acknowledge that inorganic carbon compounds, like carbonates, cannot contribute to stable formation and will not persist in the soil for a long time. To handle this, the ratios of hydrogen and oxygen are preferably related to the organic carbon

(C_{org}) (Budai et al., 2013). However, the measurement of organic carbon instead of total carbon is rather rare in the literature (Leng et al., 2018). Moreover, the influence of the inorganic carbon is only possible if the ash content is high, and will not influence calculations for a biochar from a woody feedstock with normal ash content, because of the typical low ash content (Enders et al., 2012).

3.2.2 Biotic and abiotic stress

Degradation of carbon when biochar is applied to soil is driven by the biological, chemical and physical processes (Mašek et al., 2013). The biotic factors that are a part of the degradation are fungus, bacteria and soil-animals and they drive the microbial degradation (Wang et al., 2016). Physical fragmentation of the biochar such as; freezing and thawing, rain and winds, roots and fungi physical interaction and bioturbation, will increase the available surface and increase the impact of the degradation (Lehmann & Joseph, 2009). Examples of abiotic factors that could affect the stability of biochar is temperature, moisture and the composition of the soil regarding clay, minerals and organic content (Wang et al., 2016). These factors could interact with the biological processes but also contribute to the abiotic processes e.g. carbonate dissolution and abiotic oxidation.

3.2.3 Physical fate of biochar in different applications

Four different applications for biochar were investigated regarding the physical fate of the carbon: biochar for soil amendment in agriculture, biochar for green spaces and tree planting in the city, biochar in consumer bag and biochar as a filler material in concrete. While claiming that biochar is a carbon sink for several hundreds of years it is relevant to spread light on where the biochar eventually will be located when put in different applications and how that location could affect the degradation behavior.

Biochar as a soil amendment in agriculture

Loss of biochar from the field topsoil derived partly from the degradation of carbon, but a substantial amount of biochar is lost by other mechanisms and should not be regarded released to the atmosphere (Budai et al., 2013). The biochar could for instance be lost through bioturbation, erosion and runoff (Wang et al., 2016). Translocation to subsoils could occur through tillage or biological interaction and bioturbation from organisms and worms (Lehmann & Joseph, 2009). Erosion is also common and due to the low density and sometimes small particles biochar is more prone to follow the wind and float away with runoff water than the soil organic compounds (Lehmann & Joseph, 2009). This is a loss of biochar from the field but not a loss of carbon sequestration. In the case of bioturbation, when the biochar is moved down to subsoils could the stability increase compared to the top soil (Larenc & Lal, 2014). The biochar that is lost through erosion and runoff will with time end up in ocean or lake sediments (Budai et al., 2012). The low oxygen environment in water saturated areas, like paddy soils or ocean sediments will increase the mean residence time (MRT) of the biochar (Wang et al., 2016). Budai et al. (2013) conclude that the dislocation of biochar from the field not threaten the carbon sink potential.

Biochar in green spaces and tree planting in the city

Biochar as a soil amendment or as a substitution to soil in the green spaces of the city is favorable both for its nutrient and water holding capacity. At Högdalen in Stockholm biochar is produced from the citizens' garden waste and used to improve green areas in the city (SVOA, 2019). In the city, it is sometimes necessary to relocate and move around the soil, in general the soil is stored until it is needed again or used as a filling material (Wibom, 2019). The movement of the soil will mix it and increase the decomposing, but not in a more extended way than tilling in agriculture. Wibom (2019) identified a risk for the carbon sequester potential is if the mass becomes heavy contaminated and need to be put on a landfill with a pretreatment of composting. That would increase the degradation rate, but this was, however, estimated to be a negligible fraction.

Biochar in consumer bags

Biochar for soil amendment in consumer bags is available on the private consumer market, e.g. the soil producer Hasselfors Garden distribute uncharged biochar in 4 l bags and Röllunda have a 40 l bag where biochar is mixed with composted poultry manure. When the biochar is unmixed with soil there could be a risk that the consumer uses the biochar as a fuel instead of a soil amendment, however, the size of the biochar is not to be mistaken for charcoal and further the price (20 SEK /l) does not encourage to use biochar instead of charcoal. When the biochar is mixed with soil, the risk for deliberate as a fuel is minimized. However, the private management of soil after it has served its purpose may differ a lot. If the consumer lives in a house with garden and old soil from pots is being exchange, the soil may be added to the soil in the garden. In that case the carbon sequestration remained at the same level as claimed. But if the consumer lives in an apartment there is a risk that the soil ends up in the solid waste that is sent to incineration, where the carbon will be lost. In a compilation of Sweden's municipalities analysis of household waste 2013-2016 made by Avfall Sverige it is reported that household waste in mean contains 2-2.5 % garden waste but how much of that that is soil is not known (Westin, 2019).

Biochar in concrete for buildings and constructions

Biochar in concrete is one new emerging market for biochar, where the biochar could be a feasible strategy to decrease the carbon footprint of buildings and materials (Andersson, 2018). There is no knowledge of how the concrete will affect the biochar stability, but since it is mixed to the material and kept out from the stress that occurs from biotic factors in soil it is assumed to be at least as stable as if it would have been mixed with soil. The life span of a building or a construction is, however, limited and the lifetime of the building will probably be shorter than the expected stability of the carbon estimated MRT. Demolition waste of concrete is commonly used in lower value filling, like road constructions (Wibom, 2019). This is, however, speculations of what we are expected to do with deconstruction materials in 50-100 years and Wibom (2019) underlines the ongoing development in the area, and that the material in the future will be reused in new constructions. The identified risk for the carbon sequestration value when biochar is applied to concrete corresponds to the small risk of heavy contamination, where the material will be destructed at a high temperature and the carbon will be released to the atmosphere (Wibom, 2019).

3.3 How stable is the carbon in biochar?

Biochar has, as described in the introduction been addressed with a wide range of different stability and individual experiments which have shown remarkably high and low estimated stability. Krusakov et al. (2014) estimate a MRT of 4 000 years while Rosa et al. (2017) found MRT values on a decade scale. This is not unexpected with respect to the wide continuum of different properties that can origin from different feedstocks and processes as previous described. Another reason for a large variety in estimated stability is the wide spectra of different methods to both measuring and modeling the data, which will be described in section 3.4 and 3.5. More or less accurate methods of measuring and extrapolate the data and different standards of duration for example time and temperature contribute to the variation of test results. Spokas (2010) points out that extrapolation of data from experiments shorter than two years to degradation over decades is unreliable and the model used to extrapolate the data will largely impact the estimated time (Leng et al., 2019). This will not change the actually stability, just the estimation of it.

An accurate estimation of how stable biochar is in general cannot be found in one individual experiment. The study and comparing of many results from different biochar can give an indication of the general stability and is recommended. However, the risk of large variations between studies is often hidden in meta-studies, constituting a challenge (Leng et al., 2018). Wang et al. (2016) conducted a meta-analysis on 128 observations, using only degradation results that had been calculated with methods that can distinguish the source of carbon dioxide and therefore separate the flux from biochar and SOM. To model the time, the double exponential model was used, that is claimed to be the most accurate model, further described in section 3.5.

The combined result from the meta-study, including all feedstocks, estimate that the MRT of the labile pool is 108 days with a size of 3 % and the remaining 97 % is the stable pool with an estimated MRT of 556 years, but the variation in MRT is large (Wang et al., 2016). This corresponds to a stability that indicate that 80 % of the sequestered carbon will remain stable after 100 years in soil. The study also found that the degradation rate from woody feedstock was more than three times slower than the mean of all feedstocks and despite large variation in individual results it was concluded that all biochar is more recalcitrant than the biomass it originates from (Wang et al., 2016).

3.4 Methods for measuring the carbon stability of biochar

The true stability of a biochar could only be revealed with a perfect measuring in the actual application in time that corresponds to the lifespan of the biochar. In terms of time and resources is that not an option. Experiment to measure the stability of biochar have challenges in the difficulties to mimic the actual conditions in a controlled environment of an incubation experiment, or manage to do proper monitoring of the natural behavior in a field trial. In this section the methods that can give data to calculate the degradation rate are described.

3.4.1 Incubation

A method to measure the carbon degradation is incubation trials where biochar alone, or in mixture with soil or/and added nutrients is studied over time regarding the flux of CO₂ from the biochar samples in a laboratory. The conditions like temperature, saturation of water and addition of nutrients are known and controlled. Important parameters that will affect the degradation are temperature, moisture and the particle size of the biochar, but also factors like oxygen level, size and type of microbes and nutrients that are added (Zimmerman and Gao, 2013). The controlled environment enables to compare how different parameters affect the degradation rate of biochar with specific characteristics.

The drawback with incubation trials is that they cannot fully mimic the natural interaction with the environment. On one hand the conditions in an incubation can be optimized to facilitate the degradation and underestimates the actual stability, like periods of less microbial activity or formation of complex aggregate in the soil that encapsulating in the biochar (Wang et al., 2016). Rosa et al (2018) states on the other hand that incubation overestimate the stability due to the lack of many interacting natural processes that cannot be simulated in an incubation. Zimmerman and Gao (2013) list the influence of freezing and thawing, UV radiation, rainwater infiltration and the present of fungi as factors in the open natural system that not will be accounted for in the incubation.

3.4.2 Field trials

Field studies provide an opportunity to study real degradation of biochar. Biochar degradation could be studied in the actual environment if the distribution of biochar and the background degradation is known (Zimmerman and Gao, 2013), but the lack of knowledge makes the understanding of biochar stability in soil sparse (Wang et al., 2016). The measuring of the actual biochar that remains in the soil is not a reliable method to estimate the degradation rate because a substantial fraction is lost through erosion, bioturbation or with runoff with water (Budai et al., 2013). How much biochar that remains in the soil is of main importance for the soil benefits, however, the carbon sequestration value is not wasted by the dislocation as described in section 3.2.3. The other option is to measure the carbon dioxide flux from the application site, then it is crucial to use a method to detect the origin of the flux so the carbon from the biochar can be distinguished from other sources (Leng et al., 2019). Leng et al. points out that field conditions are so complex that parameters that have been stated as key influencers in one study has in other studies turned out to be negligible.

3.4.3 Other methods

The field and the incubation trials are time and resource demanding and there have been efforts to connect the characteristics of a natural aged char with the effect that can be observed by chemical aging. Cross and Sohi (2013) developed a method where chemical aging would mimic the natural degradation of biochar with known age, possible to conduct within days. The method is more closely described in section 3.6.1. together with other methods that is possible to use to indicate stability. One other way to utilize chemical aging is to shortening the duration time by removing the easy degradable labile fraction (Leng et al., 2019).

3.4.4 Best practice for experimental design

The current lack of standard to aim for an accurate estimation of the stability contributes to the mixture of different results with many unknown co-variables (Leng et al., 2018). This makes the result difficult to compare and the reproducibility low and to interpret this results without specialist knowledge is difficult (Leng et al., 2019). Wang et al. (2016) found that modeled MRT from studies longer than 1 year in mean was 4 times longer than MRT from studies shorter than 0.5 year. Duration time for the experiment is an important factor for the result, longer trials tend to be more accurate because the rapid degradation from the small labile pool has less influence on the result. Short term tests will mainly focus on the flux from the small labile pool and may underestimate the actual stability in soil (Sing et al., 2012). Leng et al. (2019) conclude that important factors for an accurate estimation of the degradation rate is to mimic the natural degradation in soil in a standard way, using at least a two year long experiment, preferably longer than three years, to properly distinguish the change in degradation behavior. Moreover, it is important to use a method that separate carbon flux from the biochar from other sources (Leng et al., 2019).

3.5 Models to predict carbon degradation over time

There are different ways to express the stability and they all depend on the modeled degradation rate, k (degradation/time) (Leng et al., 2019). The degradation rate, k is used to express and communicate the stability in different ways. The mean residence time (MRT) meaning how long the carbon in average stays stable in the system is calculated according to equation (1), the halftime ($BC_{t1/2}$) referring to how long time it takes to lose 50 % of the carbon is calculated according to equation (2) (Leng et al., 2019). The BC_{+100} express how large fraction of the carbon that will remain 100 years after application ($t = 100$) shown in equation (3), (Cross and Sohi 2013).

$$MRT = 1/k \quad (1)$$

$$BC_{t1/2} = \ln 2 * MRT \quad (2)$$

$$BC_{+100} = 100 e^{-kt} \quad (3)$$

Different models (described in the subsections) can be used to fit the data from a field or an incubation to a model to estimate the degradation rate. The result may differ depending on the model thanks to the grouping of degradation behavior. In the case of several pools is the degradation behavior is described for each individual pool. In general, it is important to be very careful when using data from short term experiments since the longest known duration is affected by the rapid degradation of the labile pool (Wang et al., 2016). The measurement of carbon flux is done during a relatively short time comparing to the time span that is to be predicted. Even the longest test by Krusakov et al. (2014) of 8.5 years is short compared to the estimated lifetime of hundreds of years.

3.5.1 1- pool model

The single pool model (equation 4) equals the BC mineralized at the time (t), meaning the carbon that has been lost from the biochar to a pool of carbon that degrade according to an exponential function. This approach assumes that all carbon molecules in the biochar have a similar degradation behavior (Zimmerman and Gao, 2013). It is a simple model to use and it only requires two known data points (Leng et al., 2019).

$$\text{BC mineralized}_{(t)} = \text{BC}_{(\text{initial})}(1 - e^{-kt}) \quad (4)$$

From known data points of initial biochar and after time (t) remaining biochar could a degradation rate k be calculated. However, this type of model has low accuracy because it utilizes the average rate for all the carbon (Leng et al., 2019).

3.5.2 2-pool model

The 2-pool model assumes that the degradation behavior could be grouped into two different pools where compounds with similar behavior are grouped. It is divided into a labile pool and one stable pool and equation (5) is used to find the degradation rate for each pool (Leng et al., 2019; Zimmerman and Gao, 2013).

$$\text{BC mineralized}_{(t)} = \text{BC}_{(\text{initial labile pool})}(1 - e^{-k_1t}) + \text{BC}_{(\text{initial stable pool})}(1 - e^{-k_2t}) \quad (5)$$

The size of the labile pool is approximately 3 % (Wang et al., 2016). This model has turned out to be useful and the 2-pool model is recommended to be used for a more accurate estimation of the degradation rate than the 1-pool model (Leng et al., 2019). Figure 3 illustrates the difference of using a 1-pool model and a 2-pool model when extrapolate the mean values of biochar degradation described by Wang et al. (2016). Despite the use of same data of degradation behavior, the extrapolated results differ a lot, the 1- pool model predict that 10 % of the carbon remains after a hundred years while the 2- pool model indicates that 80 % of the carbon remains stable after a hundred years.

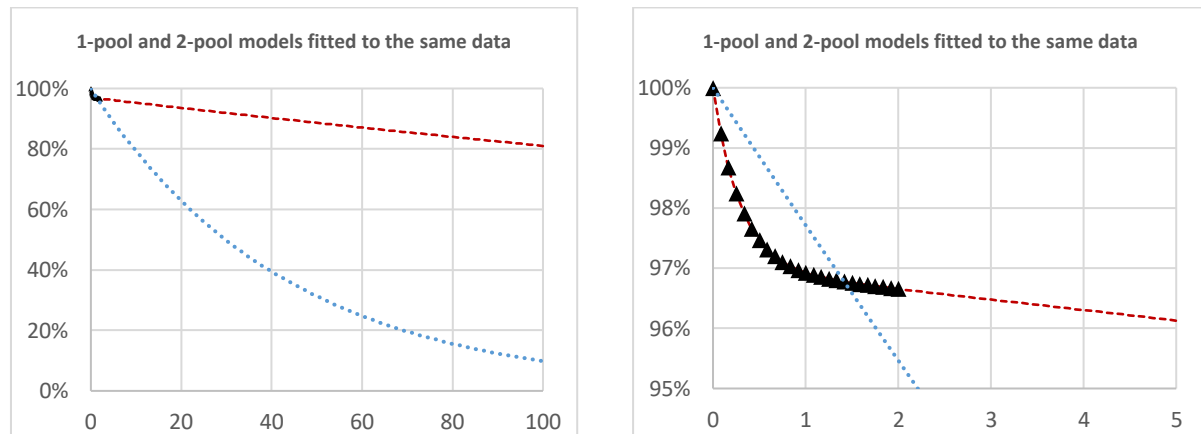


Figure 3 illustrate the variation of estimated stability depending on the model that is used to extrapolate the observed degradation behavior. Left: 100 years and right: 5 years. Mean values described by Wang et al. (2016) modeled with 1-pool model (blue) and 2-pool model (red).

3.5.3 Multi pool models and the power model

The 2-pool model could be extended by further dividing the carbon into pools of more recalcitrant carbon, this would increase the estimated stability but the approach requires a lot of data to be well fitted (Leng et al., 2019). The power model is probably the one model that approaches the degradation rate in a theoretical satisfying way, reflecting the continuum of different degradation behavior that is expected in the biochar. In the power model in equation (6) the degradation rate decreases with time (t), the slope

(m), intersection (b) and the initial carbon (C_0) can be integrated to calculate the loss over time, in detail described by Zimmerman (2010).

$$\frac{dC}{dt} = -C_0 e^{bt^m} \quad (6)$$

However, even if the power model along with the multi-pools model seems to be the most accurate modeling approach it need large amount of data and longer trial durations. The complexity of the models and mathematical restrictions preventing them to be commonly used for stability assessment (Leng et al., 2019).

3.6 Methods to indicate and predict the stability of biochar

With incubation and modeling, described in previous sections, the degradation behavior for a biochar can be estimated. To avoid being forced to repeat this resource demanding process for every batch of biochar is it necessary to correlate the property of the biochar to the modeled stability and connect a degradation behavior to a biochar characteristic. Leng et al. (2018) defined two categories of methods that can connect a direct recalcitrant behavior or molecular structure to a biochar with estimated stability; analysis of the carbon structure and analysis of the biochar oxidation resistance. An overview of the different categories and methods can be seen in table 1 and the methods are described further in the subsections.

Table 1. Methods that could be used to indicate stability.

Analysis of the carbon structure			Analysis of biochar carbon oxidation resistance		
Ultimate analysis	Structural analysis with instrumental methods	Structure analysis with molecular markers	Proximate analysis	Thermal degradation	Chemical accelerated aging
H/C O/C Van Krevelen	NMR RXD NEXFAS XPS FTIR NIRS/MIRS	PAH BPCA Lipid analysis N Alkene analysis PY-GC-MS HY-PY-GC-MS Carbon structure analysis by He pycnometry	FC VM	TOP R50 GS	Edinburgh stability tool H2O2 Potassium dichromate oxidation Permanganate oxidation Extraction methods

3.6.1 Analysis of the carbon structure

3.6.1.1 Ultimate analysis

The ultimate analysis aims to determine the elemental composition of a material, e.g. N, H, O and C (Liu, 2011). The elemental composition is indicative for the aromaticity and there for a possible indicator for carbon stability (Leng et al., 2018).

H/C

The ratio between the amount of hydrogen and carbon in the biochar can indicate the degree of aromatic condensation and how much of the carbon that form the more stable structures through the abundance of double carbon bounding (Leng et al., 2018). The ratio has strong correlation to modelled MRT (Budai et al., 2013). The method of using H/C as an indicator is based on elemental analysis, which is an accessible and relatively fast and cost effective analysis for a biochar producer (Leng et al., 2018). Budai et al. (2013) proposed a system that indicates the stability based on the H/C_{org} ratio, expressed as BC_{+100} ,

indicating how much of the initial carbon that is remaining after 100 years. The BC_{+100} index presented in Budai et al, (2013) builds on MRT values modeled by the double exponential method in two different studies and 31 observations (Zimmerman, 2010; Sing et al., 2012) and the analysis of different methods by an expert panel. Budai et al. (2013) aggregated a model of the data expressed as a linear function $BC_{+100} = -74.3 H/C_{org} + 110.2$ in the range $H/C = 0.4- 0.7$ seen in fig 4a with the 95% confidence interval marked. IBI (2018) interpret the model of the test results to a stepwise estimation on the stability at ratios of 0.4 – 0.7, seen as green bars in figure 4b.

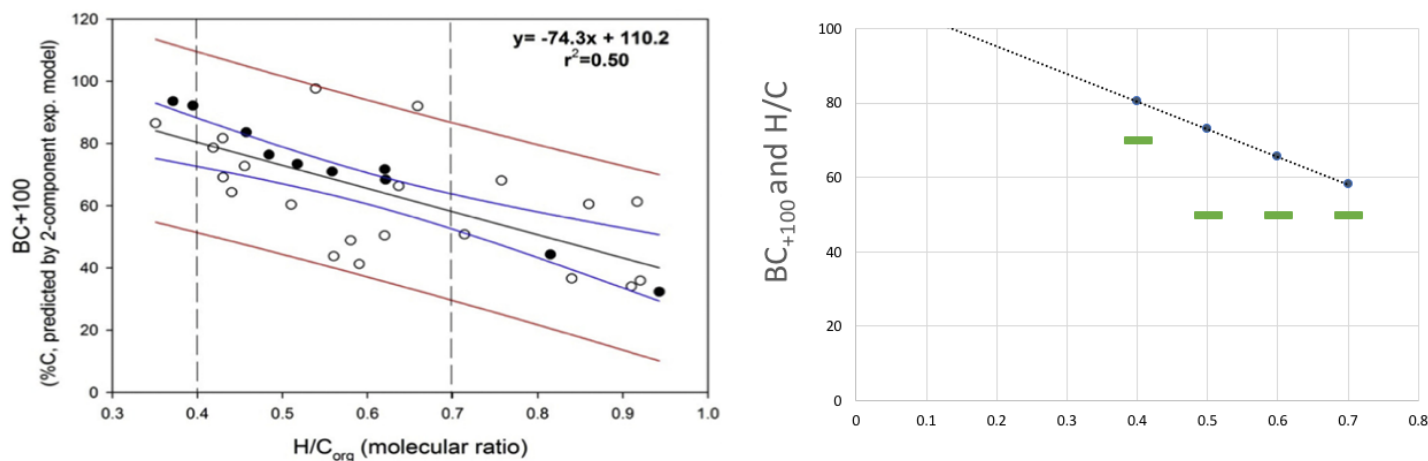


Figure 4. (a) the data points, mean value (black line) and 95 % confidence interval (blue) and prediction interval (red) reprinted from Budai et al. (2013). (b) a linear trend of the mean values and IBI interpretation of a conservative cut of values.

IBI acknowledge the need of a supplementary method that would analyze the ash fraction because the high ash biochar seem to provide an inaccurate result, and overestimate the stability. The expert panel concluded that an upper limit should be restricted to 80% ash in the biochar to use the method. It was concluded for the use of the BC_{+100} that no complementary method was needed since the IBI definition of (class) biochar require at least 60 % organic carbon (Budai et al., 2013). Furthermore, the expert panel did stress that this model is very conservative and that it should be developed and calibrated according with new knowledge and research.

The H/C method as proposed by Budai et al. (2013) seen in figure 4a, is still used by IBI. Smith (2019) proposed that the model should be used as a stability indicator in a seminar that presented the proposed development of a business model/framework to create a carbon offset protocol. Leng et al. (2018) points out that the properties alone cannot capture the entire dynamic of the mineralization rate and that the relationship between H/C and BC_{+100} does not give a precise estimation of the stability. However, the estimated stability indicating BC_{+100} 50 % and 70 % (Figure 4b) is conservative and improvements and more developed methods could give a more precise estimation (Leng et al., 2019). The H/C method as an indicator has thanks to its availability and simplicity been widely accepted and has besides the use in IBI also been adopted by European Biochar Certificate (EBC, 2012).

O/C

The ratio of oxygen compared to carbon as an indicator of carbon stability builds on the same idea as hydrogen as an indicator (Budai et al., 2013). A low ratio of oxygen in the biochar indicates a higher content of aromatic current structures and less carbon that participate in more reactive molecules such as functional groups and volatiles. Spokas (2010) points out that O/C is a function of highest treatment temperature, feedstock and other factors and will there for be a better indicator of carbon stability than

the actual production parameters. Spokas (2010) used data from 35 observations to propose an indication of carbon stability expressed as halftime ($BC_{t1/2}$) connected to the O/C ratio (Table 2).

Table 2. The range of stability connected to the O/C ratio, adapted from Spokas (2010)

O/C ratio	Range of indicated stability ($BC_{t1/2}$)
> 0.6	100 years
0.2-0.6	100 - 1000 years
< 0.2	1000 years

The use of O/C_{org} ratio of maximum 0.4 in combination with H/C_{org} ratio is adopted by the European Biochar Certificate (EBC) the voluntary industry standard in Europe, as an indicator of stability (EBC 2012). In the EBC standard the labeling of the biochar is, however, obligated to just declare H/C ratio where an upper limit to be classified as biochar is 0.7 (EBC, 2012).

The method for establish the content of oxygen constitute a challenge because to conduct a direct analysis of oxygen is rare (e.g the XPS method) and the common method is to calculate the O/C content from an elemental analysis $O = 100 - C - H - N - S - ash$ (W%). This constitute a risk for overestimation and has therefore been dismissed as reliable method (Budai et al., 2013).

Van Krevelen diagram

A Van Krevelen diagram is the combination of O/C and H/C ratio, traditionally used for coal and petroleum and commonly used to show the differences in the material from the biomass feedstock. The diagram can characterizes different organic materials according to its content of oxygen and hydrogen and its evolution during the pyrolysis process (Leng et al., 2018). The spectra of different material from the natural carbonization process range from anthracite with typical low ratios of both H and O, to the opposite side where biomass and cellulose has a high H and O ratio. Weber and Quicker (2018) constructed a Van Krevelen diagram with 212 different organic materials treated at different temperatures, and a clear relation between the decreasing ratios and higher treatment temperature is shown, especially for woody feedstock. The use of both O/C and H/C ratio are in line with EBC certification system as mentioned in the previous section. However, there is no direct relation to estimated time of degradation and as previous stated, the direct analysis of oxygen is not an accessible method (Leng et al., 2018).

3.6.1.2 Structural analysis with instrumental methods

In this section the methods seeking knowledge of the biochar structure with the use of different instrument is presented. There is a strong relationship between the mineralization rate of the carbon and the aromaticity and the degree of aromatic condensation in the biochar (Leng et al., 2018). The aromaticity refers to the extent of aromatic carbon in relation to the non-aromatic carbon in the material and the degree of aromatic condensation to the size and quality of the aromatic compounds. Several possible methods to determine the aromatic and /or the degree of aromatic condensation and its potential to constitute a reliable indicator for stability are described below.

Nuclear magnetic resonance analysis (NMR)

NMR is commonly used within organic chemistry due to its ability to identify and characterize molecules. The method relies on detecting and analyzing the trace of energy the dipolar molecules emit with changing magnetic field (Willard, 1988). Solid state ^{13}C NMR use the dipolar ^{13}C isotope to estimate the aromaticity and degree of aromatic condensation by estimating the average size of the aromatic clusters (Nguyen et al., 2010). Sing et al. (2012) demonstrate a strong relation between both aromaticity and degree of aromatic condensation found by NMR and the modeled MRT from a 5-year incubation experiment. Leng et al. (2018) state that NMR is a promising indicator of stability but acknowledge the further need of validation of the relationship with modelled MRT. The method also

struggles with the practical challenge of the differences between NMR equipment. This could in some extent be solved by introducing a standard set of biochar to use for calibration (Leng et al., 2018).

X-ray diffraction (RXD), Near edge X-ray absorb fine structure (NEXAFS) and X-ray photon spectroscopy (XPS)

RXD is an analysis of the three dimensional structure of the material, where the crystalline and well organized structures can be identified by the diffraction pattern that is emitted from the X-ray (Willard, 1988, p 372). Every substance has different patterns and gives therefore a unique fingerprint for the structure of complex organic compounds. This method could be useful for determine the aromaticity of a biochar with a high crystallinity, but is not suitable for determining aromaticity of a wider range of temperatures and the method need also further validation (Leng et al., 2018).

NEXAFS analyze the aromaticity and the degree of aromatic condensation by the functional groups and the detection of characteristic carbon double bounds and it has been used to assess the stability of black carbon in soil with organic origin (Liang et al., 2008). The result when using it to characterize biochar regarding aromatic and degree of carbonization is, however, not consistent (Sing et al., 2014) and it may be biased from resonance and it need further validation. Furthermore, is it according to Leng et al. (2018) not a sensitive method for low HTT biochar and an expensive method.

XPS is a method that detects the energy that is emitted when a molecule or an atom is exposed to high energy X-ray, depending on the internal binding energy in the core can different levels of energy be detected (Willard, 1988). XPS can be used to indicate stability by determine the ratio of unoxidized and oxidized carbon and functional groups (Liang et al., 2008). The method could also be used to directly indicate the ratio of O/C, which the elemental analysis cannot cover. However, the method can mainly detect surface compounds and will address the short term stability of biochar. Furthermore, it is an expensive method that would need validation to constitute a stability indicator (Leng et al., 2018).

Fourier transform infrared spectroscopy (FTIR) and Near/Mid infrared diffuse reflectance spectroscopy (NIRS/MIRS)

FTIR is used to analyzing the decrease of aliphatic compounds and functional groups that are typical less stable, in relation to the more aromatic compounds. The infrared spectra is used to analyze structures and compounds by utilizing the motions and vibrations ability to absorb specific wavelengths of the infra-red spectra (Willard 1988). This is a more frequently used method to assess the presence of functional groups than XPS. The method compares the relation between functional groups and aliphatic hydro carbon, which contains more oxygen than the aromatic hydro carbon with stabile double bound carbon (Leng et al., 2018). This is a qualitative method that with validation could have potential as a complementary method.

NIRS/MIRS infrared diffuse reflectance spectroscopy in near- or mid-infrared spectral range can be used to determine the carbon content in soil, and has shown to give good estimation on fixed carbon and volatile matter (Andrade et al., 2012). Common for the methods using infrared is that they are qualitative, and could possibly be supplementary methods but has a need for further validation (Leng et al., 2018).

3.6.1.3 Structure analysis with molecular markers

Methods that aims to analyze the structure of the biochar with molecule markers is presented in this section. The structure of carbon is closely related to stability (Leng et al., 2018).

Polycyclic aromatic hydrocarbon (PAH)

PAH as a molecule marker to indicate the structure is often used to differentiate pyrogenic material from fossil carbon in soil but has could also be used as a stability indicator (Wiedemeier et al., 2015a). The analysis of PAH is done through gas or liquid chromatography and accounts for the different sizes of aromatic ring structure. A drawback with the method is that very stable hydrocarbons are not extractable

and cannot be detected by chromatography and therefore this is not a suitable method for biochar produced at a higher HTT where the result will be inaccurate (Leng et al., 2018).

Benzene poly carboxylic acid (BPCA)

The detection of BPCA is a method to analyze the more complex carbon structures than the sole aromatic hydrocarbons and is widely used to quantify carbon in soil, sediment and charcoal (Wiedemeier et al., 2015a). The compounds are digested into monomers and can then be detected by gas or liquid chromatography, the BPCA pattern that indicate the original polycyclic structure, that could indicate the stability of the carbon compounds (Leng et al., 2018). McBeath et al. (2011) found a correlation between the degree of aromatic condensation, analyzed with NMR, and the analysis of BPCA. However, there is a problem with the method since the most stable compounds are also recalcitrant to chemical degradation. A larger fraction of carbon compounds remains unsolved and is therefore undetected if the biochar has a high stability. In practice this mean that it is a functional method for biochar's with a $\text{HTT} < 700^\circ\text{C}$ but might underestimate the stability for a more stable biochar (Leng et al., 2018). BPCA could be a viable method in combination to an elemental analysis but there is a need of optimization (Budai et al., 2017; Leng et al., 2018).

Lipid and N-alkens analysis

Using Lipid analysis and analysis of N-alkanes has also been proposed as a molecular marker since a decreasing trend could indicate an incremental aromaticity. Wiedemeier et al., (2015a) investigated both lipid analysis and N-alkans as a function of HTT but concluded that there was no reliable pattern. Both methods are inaccurate at a higher process temperature (Leng et al., 2019).

Pyrolysis GC-MS and Hydro Pyrolysis-GC-MS

Pyrolysis GC-MS is a method that builds on further pyrolysis of the biochar, more intense than the production process. The pyrolysis product is analyzed with gas chromatography and mass spectroscopy, with the aim to analyze the original compounds and chemical composition of the biochar. Detected compounds like bensofuran and polyzaccharids are a molecular marker for cellulose and holocellulose while phenols and guaiacols corresponds to lignin and naphthalene marks poly condensed aromatic structures (Conti et al., 2014). The proportion of labile and stabile compounds detected could be estimated and the method could indicate the carbon stability but there is a need of validation (Leng et al., 2018). Conti et al. (2014) found correlation with the H/C ratio in several studies. Thermal stability indices (TSI) is an index described by Suárez-Abelenda et al. (2017) that grade the stability on a 0-100 scale based on the relative abundance of stable compounds and could be developed to an indicator. However, the pyrolysis method for stability assessment has a drawback because of the small amount of detectable compound found in the most stable biochar's typically produced at a high HTT and is not reliable for highly carbonized biochar (Kaal et al., 2012).

The Hydro Pyrolysis described by Rombolà et al. (2016) is a more robust method that estimate the labile and stabile content in the biochar. The method is similar to the one previous described but the pyrolysis is done during high pressure in hydrogen and facilitated by a catalyst. Results from the method has been strongly invers correlated to H/C ratio and this might be a promising method but it needs further validation (Leng et al., 2018). It was also concluded that it is a complicated method and could be expensive, which make it unsuitable as an easy access indicator.

Carbon structure analysis by He pycnometry

This is a simple physic method that independent analyses that utilizing helium to penetrate all the pores in the biochar to determine the skeletal density. This could indirect give an estimation of the carbon condensation and a correlation to the degree of aromatic condensation was found for biochar produced at $\text{HTT } 300\text{--}1000^\circ\text{C}$ by Wiedemeier et al. (2015b). Leng et al (2018) conclude the method to be simple and cost effective, but current experience on the method is low and need to be extended and validated in order to be a possible indicator of carbon stability.

3.6.2 Analysis of biochar carbon oxidation resistance

The carbon stability in biochar can be evaluated according to how well the biochar resist thermal and chemical oxidation.

3.6.2.1 Proximate analysis

The proximate analysis determines the biochar mass content of: moisture, volatiles, fixed carbon and ash by using a standard method (Liu, 2011). The British/European standard (BS EN 14775:2009) stipulates the moisture content as the loss of weight when drying the sample in 105°C and the further weight lost that occurs during 7 minutes in 900°C is denoted as the volatile matter (VM). Fixed carbon (FC) and the remaining ash, are determined by combustion of the residues according to the standard.

Fixed carbon (FC) or/and Volatile matter (VM)

FC increase with HTT and could be an indicator for stability and FC content has shown correlation to aromatic C content, stable C content and O/C ratio (Leng et al., 2018). In contrast to FC, VM represents the more rapidly degradable carbon and is closely related to the labile carbon fraction. VM content will affect the estimated stability in an incubation test and will contribute to the initial short term degradation, however, there is no correlation found between VM and modeled half-life (Spokas, 2010). Since FC and VM are given as a fraction of the entire biochar is it not a good method for comparing stability of different biochar (Leng et al., 2018). Spokas (2010) proposed a combination of O/C, H/C and VM as an indicator of the carbon sequestration value of a biochar, where a higher proportion than 80% VM (ash free) has no sequestration value, but this method must still be better verified (Leng et al., 2018). A more accurate way to use the approximate analysis is to combine the VM and FM to the ratio VM/FC. Klasson (2017) demonstrate a correlation to results from elemental analysis, making it possible to estimate the ratio of O/C and H/C based on the VM/FC content. Further quotes can be calculated and there is correlation to both stabile carbon content, aromatic carbon content and the method is by Leng et al. (2018) considered as a possible supplementary method because of the strong correlation with other indicators. However, the method to determine fixed carbon relies on calculations based on assessment of volatiles according to $FC = 100 - (\% H_2O + \% VM + \% Ash)$ and may be overestimated and the condition variation for the proxy analysis may affect the result (Leng et al., 2018).

3.6.2.2. Thermal degradation

The stability could be related to what extent the carbon in the biochar can persist thermal oxidation. The use of oxidation in a favorable environment is commonly used to examine oxidative stability in other materials, and because of the optimized oxidation environment, it could be a good method for stability assessment of biochar (Leng et al., 2018).

Temperature programmed oxidation (TPO), recalcitrant index (R_{50}) and gained stability (GS)

The TPO relies on weight loss in different temperature intervals where the fraction that is lost between 30 and 200°C corresponds to the volatile organic carbon, 200 to 380°C reflecting the labile carbon content, 380-475°C the recalcitrant organic carbon, 475 – 600°C refractory organic carbon and 600-1000°C mainly inorganic carbon, such as carbonates (Leng et al., 2018). The method is commonly used to assess fuels like biodiesel and the controlled environment in the method might be good for the analysis of biochar. The method could provide information of the relative stability but the actual mechanism of degradation of carbon in biochar is not clearly related (Leng et al., 2018).

Harvey et al. (2012) proposed a recalcitrant index, R_{50} that addresses the relative recalcitrance of a material in relation to graphite. According to: $R_{50} = T_{50,x} / T_{50,graphite}$, where the $T_{50, x}$ represent the temperature where 50% of the carbon oxidize. A strong relationship was found in a one-year incubation test and based on this an index for stability was developed (Harvey et al., 2012). The method is according to Leng et al. (2018) a promising method, it is cost effective and easy but needs further optimization and development and the classification system must be validated. A development of the method that may increase the accuracy is the modified Recalcitrant index, Gained Stability, described by Gómez et al. (2016) as: $GS = (R_{50,x} - R_{50,CELL}) / (R_{50,PCELL} - R_{50,CELL})$, where $R_{50, x}$, $R_{50, CELL}$ and $R_{50, PCELL}$ are the R_{50} values of biochar, cellulose and cellulose char produced at HTT 750 °C for 1 h, respectively. The method

shows strong correlation to the result of chemical aging test and could increase the accuracy of R_{50} , but it needs to be validated (Leng et al., 2018).

3.6.2.3 Chemically accelerated aging

The adding of different chemicals aims to simulate the natural oxidation of biochar and could be a time efficient method to evaluate the stability of carbon in biochar by degrading the labile carbon with chemicals (Leng et al., 2018).

Edinburgh stability tool

Cross and Sohi (2013) developed a method that simulates the degradation of carbon when biochar is applied to soil that is claimed to be comparable to an application in temperate soil for a hundred years. The method is to expose the biochar to 80°C for two days and 5% hydrogen peroxide (H_2O_2). The stability is then defined as the fraction ($\mathcal{A}$) of carbon that persist the treatment according to: $\mathcal{A} = B_r * B_rC * 100\% / (B_t * B_tC)$, where B_tC and B_rC represent the carbon content in the total and residual biochar respective and B_t and B_r the mass before and after the treatment (Cross and Sohi, 2013).

The connection to time is found by comparing the mass loss over time in biochar from natural wildfires where the chemical treatment claims to be equivalent to 92 and 187 years, depending on the mean temperature (10°C respectively 7°C) of the biochar application (Cross and Sohi, 2013). The accelerated aging method captures the physical constrains that effects the stability that other methods like elemental ratios do not capture. Furthermore, it does not have to rely on models for extrapolation of short term incubation test data (Cross and Sohi, 2013). Crombie et al. (2013) found correlation with estimated stability with Edinburgh stability tool and pyrolysis temperature and the method is found to be a reliable tool determine long term stability in soil (Mašek et al., 2013). Leng et al. (2018) points out this method to be a promising method for predicting and quantifying the stability of biochar from different feedstocks. However, there is need of validation, in particular the assumptions of natural wildfire charcoal have the same behavior as the produced biochar but also that a certain amount of H_2O_2 corresponds to a specific time. Leng et al. (2019) underlines also that it is not easy to correlate oxidative stability to biotic stability of biochar.

Dichromate and Permanganate oxidation and extraction methods

Chemical aging methods could also be conducted without heat treatment, there has been tests with potassium dichromate oxidation or permanganate oxidation (Calvelo Pereira et al., 2011). The oxidation with both dichromate and permanganate have shown correlation to elemental ratios of H/C and O/C. This could be promising methods due to the easy method and low cost (Leng et al., 2018). However, the methods are currently lacking validation and the sample pool is too small to be indicative. There are also some extraction methods, based on hot water extraction or extraction with acid and base that has been tried for the purpose to indicate stability but the method has so far not provided any useful data (Leng et al., 2018).

3.7 A summary of methods indicating carbon stability

Leng et al. (2018) points out that a viable method to indicate carbon stability in biochar should be robust, repeatable and have a clear relationship with the degradation behavior. Furthermore, it should be available in laboratories, cost effective and rapid. In Table 3, the available methods are evaluated according to the criteria regarding the methods relevance and accuracy, availability and usefulness.

Some of the methods are lacking potential to be a relevant indicator and therefore not further evaluated (Table 3). Furthermore, there is a large variety of how suitable the methods are for the purpose to be a viable method for biochar producers. Some of the methods have given an inaccurate result or are just valid within a part of the possible range of materials and some methods have a large need of development and validation or lacking availability. Methods such as Edinburgh stability tool, H/C, NMR, Gained Stability and R_{50} appear to be promising for indicating carbon stability. A challenge for those promising

methods are to validate and calibrate the connection of the relative stability to an estimated time of degradation.

Table 3. Summary of the methods that has been identified as possible stability indicators. The viability is evaluated according to five criteria.

Method	Does the method have potential to provide an accurate result for the relevant range of carbon structures?*	Available for biochar producers in terms of time and cost ?	Is there a relation with measured MRT well declared?	Is it partly validated?	Acceptance? /in use? Adopted as a stability indicator?
H/C	yes	yes	yes	yes	yes
O/C	yes	no**	yes	yes	yes
Van Krevelen	yes	yes	no	yes (but not in relation to MRT)	no
NMR	yes	no (need standards)	yes	yes	no
RXD	no	-	-	-	-
NEXFAS	no	-	-	-	-
XPS	yes	no	no	no	no
FTIR	yes (maybe as a complement)	no	no	no	no
NIRS and MIRS	yes (maybe as a complement)	no	no	no	no
PAH's	no	-	-	-	-
BPCA	yes (but not reliable >700°C)	no	no	yes (compliment to ultimate analysis)	no
Lipid analysis	no	-	-	-	-
N alkene analysis	no	-	-	-	-
PY-GC-MS	no	-	-	-	-
HY-PY-GC-MS	yes	no	no	yes	no
He pycnometry	yes	yes	no	no	no
FC	yes (VM/FC could be a supplementary indicator)	partly**	no	yes	no
VM	no	-	-	-	-
TPO	yes	yes	no	no	no
R ₅₀	yes	yes	no (relative)	yes	no
Gained stability	yes	yes	no (relative)	yes	no
Edinburgh stability tool	yes	yes	no (Æ)***	yes	yes
Potassium dichromate oxidation	yes	yes	no	no	no
Permanganate oxidation	yes	yes	no	no	no
Extraction with water or acid/base	no	-	-	-	-

* The other questions are not relevant if the answer is no. ** Calculated from other analysis and relies on assumptions of the content. *** Æ is the fraction of the carbon that persist the chemical treatment.

4 Result and discussion

This section is divided in two parts that correspond to the two questions: *What is the best available method to indicate and quantify carbon sequestration potential, suitable for biochar production in the context of climate mitigation?* and *What carbon sequestration potential can be expected from Stockholm Exergi biochar project?* The first section 4.1, present the result of the best suited method and the method is further scrutinized and tested and in section 4.1.1. From this result the practical use, communication and robustness of the method is discussed and further development of the carbon stability assessment is proposed in the following sub sections. In the second part 4.2, the carbon sequestration potential of Stockholm Exergi and necessary requirements on the application is declared. The practical use and implications of different interpretations of the model is further discussed.

4.1 A viable method for indicating carbon stability

H/C_{org} with the stability communicated as BC₊₁₀₀ emerged to be the best current available method to indicate carbon stability in biochar due to its close relation to measured degradation from incubation, its acceptance and availability. As described in the previous section, there are many parallel paths and different methods that in theory have the potential to indicate the carbon stability of biochar. Despite this, the current available research is not providing enough knowledge to fully support a method to be “perfect” and the knowledge of biochar degradation is limited (Leng et al., 2018; Wang et al., 2016). However, the purpose of this work is not to find the ultimate method but a method that is robust enough to be used by biochar producers at the current state of knowledge, to estimate and account the carbon sequestration potential of the biochar. Four methods showed good potential to be useful, albeit with some improvements, as seen in the third column in table 4.

Table 4. Grouping of methods in the categories: Not viable for the purpose, Some potential but need validation and improvements and Good potential to be a useful method with some improvements.

Not viable for the purpose		Some potential but need validation and improvements		Good potential with some improvements
RXD	PY-GC-MS	BPCA	O/C	H/C _{org}
NEXFAS	VM	He pycnometry	Van Krevelen diagram	NMR
XPS	FC	HY-PY-GC-MS	Potassium dichromate	R ₅₀ and Gained stability
PAH's	Extraction with water or	VM/FC	oxidation	Edinburgh stability tool
Lipid analysis	acid/base	TPO	Permanganate	
N alkene analysis		FTIR	oxidation	
		NIRS and MIRS		

4.1.1 Test of the H/C method

The accuracy of the H/C method was tested with existing data. When data that derives from models that is acknowledge to provide a reliable result was used, the test seems to support that the H/C method is a functional and reliable indicator of stability in biochar.

Data from fifteen individual samples of biochar with an estimated MRT and a declared H/C ratio, was found in the compilation made by Lehmann & Joseph (2015). BC₊₁₀₀ was calculated from MRT and plotted with H/C. In figure 5a the result of all data points regardless of used method to model the MTR is shown. In figure 5b the data points with MRT is relying on 2-pool (or more) shown, together with the BC₊₁₀₀ model (se figure 4). The test contains too few data point to support any calibration or validation of the model. Despite this, the result, support that the BC₊₁₀₀ is a reliable indicator, but more data is needed to further strengthen the relation.

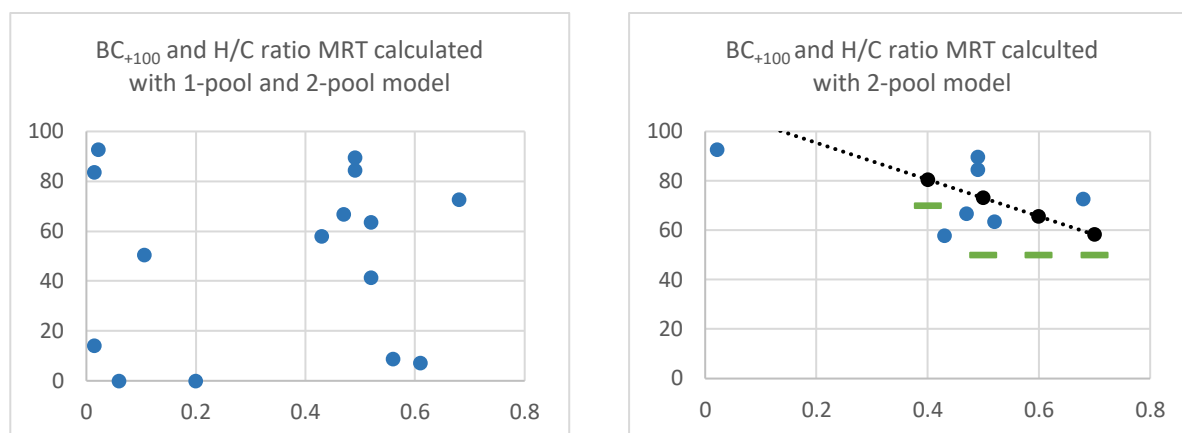


Figure 5. (a) Biochar data with modeled MRT and H/C found in literature listed by Lehmann & Joseph (2015). (b) Biochar data with modeled MRT, except result from single pool model, and H/C found in literature listed by Lehmann & Joseph (2015). The black line represents the linear trend of mean values from the study presented in Budai et al. (2013) and the green bars represent IBI's interpretation of the model into a conservative cut of values.

Leng et al. (2019) concluded that MRT preferable is modeled with the 2-pool exponential model (described in section 3.5) and that a single is not suitable to make an accurate estimation of MRT. Therefore, biochar with MRT based on extrapolation with single pool exponential function was excluded. The remaining 7 data points can be seen in figure 5b were also the original BC_{+100} , model proposed by Budai et al. (2013) is shown with black line and green bars. The MRT was calculated to BC_{+100} according to $BC_{+100} = BC_0 e^{-kt}$ and $MRT = 1/k$. For a comprehensive description of the test method, reference studies and calculations, see the method section 2 and appendix 1.

4.1.2 The robustness and use of H/C ratio and the BC_{+100} index

The development of the BC_{+100} index is claimed to be done with a conservative approach regarding assumptions made and adjustments of calculations (Budai et al., 2013). On the other hand, the calibration relies on just 31 tested biochar from 2 different studies. According to Leng et al. (2019) there is a need for further testing and calibration of the method. This need of development was already acknowledged by Budai et al. (2013) when the method was constructed. During the analysis done here of the BC_{+100} method, it emerged that the actual elemental data that the method builds on is not published, just the range of values. In contact with Zimmerman (2019), author of one of the articles behind the model, it was confirmed that elemental analyses were conducted and that the BC_{+100} index builds on direct relation between modeled MRT and the H/C ratio. The method seems to have been constructed in a good way but further development, calibration and validation are lacking.

The question of how accurately the BC_{+100} index fits with modeled MRT remains unanswered in the literature. Since its construction 2013 there is no (found) attempt to calibrate or test the method with new data although research results have accumulated. A possible explanation for that is the complexity of the system perspective on biochar; Zimmermann (2019) notes that the H/C method cannot fully cover the variation that occurs from all different feedstocks and that it does not include priming and other factors that are needed to reflect the total climate value. The test, in this study, with biochar data with known H/C ratio and modelled MRT supports that H/C ratio correlates with MRT (figure 5b). The variation seen in figure 5a is expected with respect to the challenge and complexity of accurate measure, model and extrapolate the MRT of carbon in biochar as described in the literature study in this report. The wide range of different approaches also leads to a wide range of MRT as demonstrated in section 3.4 and 3.5. The connection to modeled time could be strengthened by further validations, testing of the methods and development of standard for equipment and biochar for testing the methods. Leng et al. (2019) also underline the importance of developing and optimizing the accuracy of incubation and modeling methods. With knowledge of how well different models, field and incubation tests describe the actual degradation of carbon, indication methods, such as BC_{+100} and H/C ratio can be calibrated and improved.

At the initial construction of the BC₊₁₀₀ method it was concluded by the expert panel that a complementary proximate analysis should be used to determine the ash content, preventing errors from high ash biochar (Budai et al., 2013). This was later excluded from the model since the constraints on ash content was covered by other regulations for IBI biochar. However, if BC₊₁₀₀ is used outside the IBI context the declaration of ash content could be important. The proposed level of maximum 80 % ash (Budai et al., 2013) seems unlikely for biochar, but could occur if high ash feedstock is used or if the pyrolysis process does not work properly (Söderqvist, 2017). It is unclear if the error in the model when analyzing high ash biochar derives from the higher amount of inorganic carbon as described in section 3.2.1. The inconsistent use of the ratio of total carbon (H/C) and the organic carbon (H/C_{org}) in the evaluation done in this report derives from the inconsistency in the literature, and the H/C_{org} is only used where it is clearly stated. Enders et al. (2012) states that the type of feedstock is the most influential of the ash content where char from animal manure and waste from food and paper mills had the highest ash content and char from woody feedstock the lowest. This means that the use of H/C (and not H/C_{org}) does not constitute a problem when evaluating results from feedstocks with modest ash content such as wood. However, to use the BC₊₁₀₀ system with confidence the ash content should be declared and not exceed 80 % and the organic carbon should be addressed rather than the total carbon. The accessibility of the method should not be affected by requiring the ash content because the same laboratory could conduct both ultimate and proximate analysis on charcoal (Eurofins, 2019).

The practical use of BC₊₁₀₀ can follow two different paths, where one relates to the “conservative and safe” and the other to the “likely potential” that is reflected by the mean value. The conservative path is to follow the values prescribed by IBI where H/C_{org} = 0.5 – 0.7 corresponds to BC₊₁₀₀ 50 % and H/C_{org} 0.4 to BC₊₁₀₀ 70%. The likely potential connects to the mean value from the study (figure 4) and indicates the probable carbon sequestration potential of a certain H/C ratio. The tradeoff between those paths is to not promise to much while not underestimating the potential of carbon sequestration. If the mean values are used as an indication, variations of factors that are not captured by the H/C ratio could cause some individual biochar to be described as more stable than an incubation and modeling would estimate. The prediction of how often the mean value would overestimate the actual stability could be investigated by testing more data that origins from reliable measuring of degradation and modeling of the result. In contrast the conservative approach of IBI is likely to underestimate the carbon capture value of biochar since the mean values are higher. One implication of being pronounced conservative is that it might lead to an ineffective distribution of resources if the potential is underestimated. A conservative approach also might lead the way for less good biochar, because if a less stable biochar could show the same result as the conservative values that stable biochar is written down to, the market value would be the same but not the climate value.

A practical challenge with the use of BC₊₁₀₀ index is that H/C ratios under 0.4 are not connected to any MTR. In the IBI interpretation the stability is assumed to stay at 70 % but according to the mean value it is tempting to assume that the stability further will increase with a decreasing H/C ratio, but there is no data to support that as the model has not yet been calibrated with H/C values below 0.4.

4.1.3 Communicate the carbon sequestration value of biochar

As described in section 3.5 there are some different ways to express the stability of biochar, the mean residence time, the halftime and the BC₊₁₀₀, where the last express how large fraction that will remain after hundred years in the application. These expressions derive from the same degradation rate and have a similar meaning. However, the communication is important for the evaluation of the carbon sequestration potential. The hundred-year perspective is accepted and well implemented in the climate mitigating context.

Concluding that the hundred-year perspective is a constructive way to communicate the stability it is also good to reflect on how biochar sequestration potential distinguish from other carbon sinks that remain for hundred years. E.g. a tree; the tree might have a larger fraction of carbon sequestration than the biochar during its lifetime, which in the 100 years-perspective makes a sequestration in biochar and

a tree comparable and the tree may even be superior, see the graph in figure 6a and 6b. However, when the trees are cut down, all the carbon will be released to the atmosphere within years for most uses. Compare that almost instant loss with the degradation mechanism of biochar. Biochar that after hundred years keeps 80 % of the carbon would according to theory after two hundred years lost just another 10 % of initial carbon, and not another 20 %, and not even ultimately 100 % as in the case of sequestration in a tree that has decomposed or been used as a fuel. This difference in total sequestration value is illustrated in figure 6a and 6b where mean values from Wang et al. (2016) have been compared with the carbon captured in a tree that assumes to lives for 100 years and then completely compose during 50 years. This long term carbon sequestration value of biochar is not well expressed with the BC_{+100} index. The stability expression MTR and $BC_{t1/2}$ have a better communication of the long term value but on the other hand the 100 year-perspective are not well communicated. The communication of the long term carbon sequestration potential of biochar should be improved to better express both the 100 year-perspective and the long term value for climate mitigation.

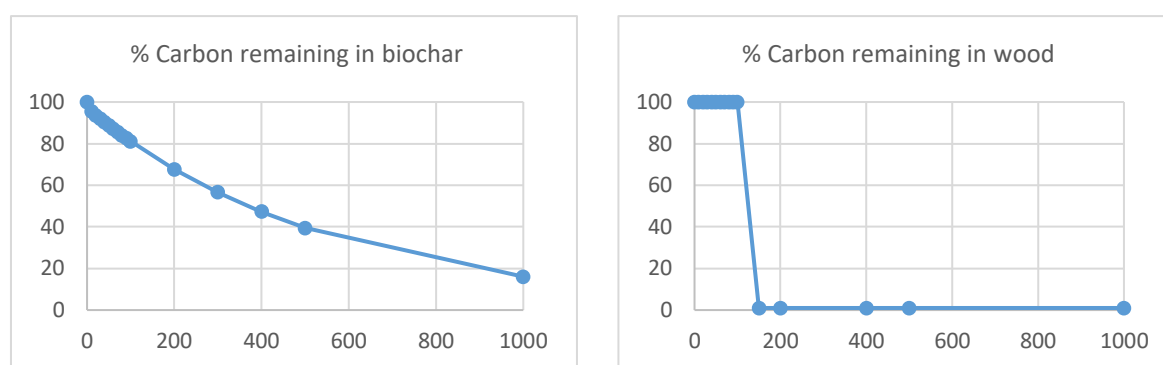


Figure 6. The different potential for carbon sequestration in biochar compared to a tree over a 1000-year perspective. The biochar degradation (a) is extrapolated with 2-pool model (equation 5) with mean values for biochar described by Wang et al. (2016). The degradation for wood (b) is modeled for a tree that stands for 100 years and then decompose completely during 50 years.

4.1.4 Recommendation to optimize the method and further research

The need of optimization and calibration of the BC_{+100} index and H/C_{org} ratio and has been outspoken both by the constructors (Budai et al., 2013) and later scrutiny (Leng et al., 2019). Further research and development could calibrate the method and give support to the model to estimated stability for H/C ratios below 0.4. Several of the other potential methods also need further validation and further research on biochar stability could also strengthen the usefulness and accuracy of other parallel methods.

Short term and rapid improvements

Test and calibration with existing data on biochar stability could be an easy and relatively fast way to improvement, comparing to new incubation trials long enough to be reliable. During the data collection for the test in this report, there were several indications that an elemental analysis was done in the experiment but the data was not published. One example is the two studies that Budai et al. (2013) builds the BC_{+100} model on. Furthermore, the list from where the references were found to the test conducted in section 4.1.1 was written in 2015 and more data could assume to have accumulated since then. There is reason to assume that a lot of unpublished data are possible to collect from different studies done on biochar stability that together could calibrate and further validate the method. If enough data is found it could also give an indication of behavior of H/C ratios below 0.4 which is currently missing in the model.

The collection of the data should be organized so that it includes relevant parameters that could have affected the MRT value making it possible to adjust and normalize the result to make it comparable. Data that is connected to MRT estimated with best practice (described by Leng et al., 2019) could then

be used to calibrate and strengthened the validity of the method. The collection of data should also be made public and accessible to other researchers to support the further development of parallel methods for carbon stability assessment and indication.

Long term development

A reliable indication method has correlation to an estimated time that has been modeled and therefor characterization of biochar in incubation is pivotal to correlate biochar properties with results from incubation and modelling (Leng et al., 2018). However, the use of this relationship depends on that the modeled time is an accurate estimation of the actual degradation of carbon. Therefor it is a priority to develop methods to accurate measure and model carbon degradation to predict and compare the carbon sequestration potential of biochar (Leng et al., 2019).

Standard methods for stability assessment is needed, both regarding analysis methods and the biochar. The many different methods currently lack standards and is therefore a mixture of different results with many unknown co-variables that makes result difficult to compare and the reproducibility low (Leng et al., 2018). Interpret this results without specialist knowledge is difficult (Leng et al., 2019). The further development of research on carbon stability in biochar would benefit of reference standards regarding biochar samples and incubation conditions. The design of the experiment and the modeling method creates considerable differences in the assessment of biochar stability and it is important that further studies follow best practice (Leng et al., 2019).

Wang et al. (2016) found out that modeled MRT from studies longer than 1 year in mean was 4 times longer than MRT from studies shorter than 0.5 year. Duration time for the experiment is an important factor for the result where longer trials tend to be more accurate because the results are less influenced by the rapid degradation of the small labile pool. Short term tests will mainly focus on the flux from the small labile pool and may underestimate the actual stability in soil (Sing et al., 2012). Leng et al. (2019) conclude that important factors for an accurate estimation of the degradation rate is to mimic the natural degradation in soil in a standardized way, using at least a two year, preferably longer than three years long experiment, to properly distinguish the change in degradation behavior. It is also important to use a method that can distinguish and separate carbon flux from the biochar from other sources.

Emerging needs of future studies:

- Reference standards, created for/possible to adjust to the Swedish condition
- Field and incubation test, preferably conducted on the same type of biochar for comparing
- Use trial time at a proper range, at least 2 years
- Use methods to separate the carbon emitted from the biochar from other sources
- Use 2-pool model (at least) to model the data.

When constructing the long term trials, make sure to simultaneously do all the analysis on the biochar that could help to support and develop other feasible methods for stability assessment and indication.

4.2 Carbon sequestration potential for the biochar project of Stockholm Exergi

The biochar project of Stockholm Exergi have the potential to each year sequester carbon in biochar that corresponding to 9 000 – 11 500 ton carbon dioxide (Table 5). The estimation builds on the capacity of the process to generate 5 000 ton biochar from 25 000 ton feedstock. The distribution of feedstock is 20 000 ton garden waste and 5 000 ton horse manure which both are available organic waste streams. The process is estimated to be available 8 000 h per year and during that time produce 40 GWh heat to the district heating system (Gustafsson, 2019).

Table 5. Estimated carbon sequestration potential per year with three different degradation rates. See appendix 2 for further details of calculation and values used.

Feedstock (ton)	Biochar yield DM (ton)	C _{org} (g/kg)	H/C _{org}	Ash (g/kg)	Sequestered carbon (stable for at least 100 years) BC ₊₁₀₀ (ton)		
					70%	80%	90%
20 000 Garden Waste	5 000	699	0.28	212	1 957.2	2 236.8	2 516.4
5 000 Horse manure		714	0.39	134	499.8	571.2	642.6
Total carbon (C):				2 457	2 808	3 159	
Total CO ₂ :				9 009	10 296	11 583	

The results in table 5 are based on example values of H/C_{org} that could be expected from the pyrolysis process. The ash content in are well below acceptable levels. However, garden waste may also be composed of different material and some might contain sand and soil from roots and therefor have a higher ash fraction. Furthermore, is the assumption that horse manure and dairy manure made due to lack of sufficient data. In a study of pyrolysis of horse manure was it shown that the molar concentration of H in frequently peaking at temperatures between 600 and 700°C (Jeong et al., 2018) and in a pyrolysis test of horse manure in Högdalen was the H/C_{org} ratio roughly 0.6 at HTT of 400°C and 0.3 for HTT at 500°C (Hemlin and Lalangas, 2018). The H/C_{org} ratio is used to indicate the BC₊₁₀₀ and expected carbon dioxide captured each year that is stored for at least hundred years. Three different approaches on how to interpret the BC₊₁₀₀ range; IBI's conservative values of 70 % for biochar with H/C_{org} ratio below 0.4, the mean value of 90 % that is expected (for H/C_{org} 0.28) if the degradation behavior follows a linear trend for H/C < 0.4. and a compromise value of 80 % that also corresponds to the mean value of biochar, regardless of H/C ratio, described by Wang et al. (2016).

Stockholm Exergi has not yet decided what pyrolysis technique to use in the biochar project. Dahlén (2019) points out that there are several ways to reach a desired product. The stability of biochar should be indicated with characteristic that belongs to the biochar and not the process, to avoid technical lock-in and ensure the stability of the biochar. However, the process and the feedstock could give a hint of the production of a stable biochar, as described in section 3.2.1.

The carbon degradation rate decreases with time and that is not well communicated by the BC₊₁₀₀ index. This gives carbon sequestration in biochar a unique long term potential which other carbon sinks, such as tree planting, lacks (se example in section 4.1.3). In practice according to the model this mean that a BC₊₁₀₀ value of 80% would correspond to BC₊₂₀₀ ≈ 70 %.

4.2.1 Confidence in the estimation

As described in section 4.1 there is not yet an obvious way to best connect the H/C_{org} value to a certain BC₊₁₀₀ value. The most conservative value indicates that 70 % of the carbon will be stable after 100 years. However, the mean of estimated stability in the model (figure 4a) and the test conducted in this report (seen in figure 5b) indicate that a higher value is likely for H/C_{org} ratios lower than 0.4. Furthermore, the meta-analysis made of Wang et al. (2016) conclude that biochar in average shows a value that is comparable to 80 % stability after 100 years and the degradation rate for woody feedstock in average has more than three times slower degradation rate than the general mean. This make the use of BC₊₁₀₀ 70 % to a likely underestimation in most cases, especially for woody feedstock with a H/C_{org} < 0.4 that dominates in this estimation. The decision on how conservative an estimation should be in contrast to the risk of an underestimation must be further discussed by decision makers within the company.

Depending on the approach and how the index is interpreted, the result of how much carbon dioxide that is possible to account for differs with 28 %. This could be an indication of the value of not just settling for reasonable functional method, but to support the development and calibration of the method to approach an indication of the correct potential and the true value, rather than the safe and conservative estimation. The current amount of data found in published literature is not enough to calibrate the method, but there is probably a lot of unpublished data that could be gathered to further support a more confident and accurate estimation of the stability.

4.2.2 Secure the carbon sequestration value in the application

The accuracy of estimation of sequestered carbon depends on the carbon being treated as intended in its application. The MRT is the stability of carbon when biochar is applied to soil. If the degradation in another application will increase compared to the soil application, it must be noticed since it might affect carbon sequestration potential. In the literature study (section 3.2.3) it was found that the environment in the application do effect the actual degradation of carbon in biochar, but the dislocation in itself does not pose a problem for the carbon sequestration value. The main risk for the carbon sequestration value is the risk of being incinerated or deliberately used as a fuel. Based on the investigation of different relocations of identified applications of biochar described in section 3.2.3 the requirements as illustrated in figure 7, are proposed to secure the sequestered carbon in its application.

In the soil application is it challenging to track the biochar since many different mechanisms will contribute to dislocation. However, the carbon sequestration value is not affected in a negative way. The use of biochar in greenspaces and as a filling in construction concrete material is also considered safe paths for the carbon sink regardless of the movement of the material in the future. The carbon sequestration is relying on an initially correct application and therefor is it necessary to specify how it is allowed to be used in the contract with the biochar byers.

The carbon sequestration potential of biochar that is distributed in consumer bags, even if it is mixed with soil, is an unsecure path since there is a risk that it will end up in the incinerated waste fraction. It is not recommended to account for the carbon sequestration detached from the product.

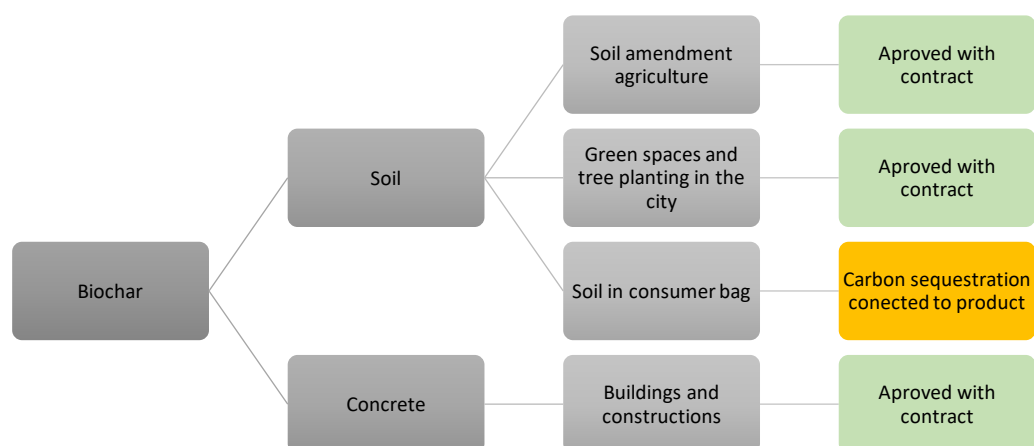


Figure 7. Overviewing the four different applications and what requirements that is needed to secure the clamed carbon sequestration value.

4.2.3 Requirements to validate that estimated carbon sequestration reflects accurate potential

The correct use of the H/C_{org} model and an approved management regarding the applications is necessary to make a confident estimation of the actual carbon sequestration and climate value of biochar. Requirements that should be fulfilled are:

- The produced biochar should initially be tested in proper intervals to ensure it maintains expected levels of hydrogen, organic carbon (C_{org}) and ash. To use the BC_{+100} model with confidence, the ash content must be in a proper range and not exceed 80 %. The intervals could be sparser when it has been shown for a longer period that the specific feedstock and production parameters generate the expected stability.
- The biochar application must be approved according to figure 7 and controlled in the agreement with the buyer of the biochar to protect the carbon sequestration value.
- If biochar is sold to be used in an application where there might be a risk for incineration or deliberate burning by consumer is it not recommended to account for the carbon sequestration detached from the product, see figure 7 and section 3.2.3.
- If a new application, not mentioned in this report, is considered the application's effect on the stability should first be evaluated.

5 Conclusions

The carbon stability is an important parameter for the carbon sequestration potential of biochar. It is not an easy task to predict the true stability due to the long time perspective, the variety in different biochar and different environmental stress in the biochar applications. Further discrepancy in the biochar stability research derives from different ways to conduct field and incubation tests and different models used to extrapolate the results. The understanding of actual stability in soil application is still sparse. The need for an accessible, robust and accepted method to estimate the carbon sequestration potential of biochar overrides the lack of complete knowledges.

There seems to be several feasible methods possible to use to indicate biochar stability, however, the H/C_{org} method and the expression BC_{+100} emerged to be the currently best available option. The H/C_{org} ratio is a cost effective and available analysis for biochar producers and has shown correlation to estimated MTR. The BC_{+100} index provides a relevant definition of the carbon sequestration potential in the context of climate mitigation and communicates the concept at a general level. However, the long term carbon sequestration value is not well communicated and the risk for underestimation of the actual value, beyond the hundred years perspective, should be acknowledged. The H/C_{org} and the BC_{+100} index should be used in combination with a proximate analysis that assure that the ash content does not exceed 80 %, because a high ash content might lead to an inaccurate indication. The practical use and interpretation of the H/C_{org} model can be done in different ways where a conservative value is BC_{+100} 70 % ($H/C_{org} < 0.4$) and 50 % ($0.4 < H/C_{org} < 0.7$). The method would benefit by further calibration and validation of the BC_{+100} index.

Estimated carbon sequestration potential of Stockholm Exergi's biochar project corresponds to 9 000 – 11 500 ton CO_2 per year depending on what approach that is adopted. The use of the conservative value of 70 % carbon remaining after hundred years for biochar with H/C below 0.4 is a safe path but will probably underestimate the actual stability. Even if this method leads to a conservative estimation that is good enough for the purpose, improvement can be done when more knowledge. In the particular case of BC_{+100} there seems to be a functional model to use now, but different approaches differ by 28 % witch motivate the further support of development of the method.

The sequestered carbon can only be accounted as a carbon sink if the biochar application does not face the risk of being used as a fuel. Applications in concrete, soil amendment on the field and biochar in green areas in the city may be relocated or lost to the surrounding. However, this is not a threat to the carbon sequestration. If the biochar is sold in bags to consumer, there is a risk for incineration and therefore should the value of the carbon sink not be detached from the product.

The method of H/C could be further validated and calibrated with data from previous studies. The long term development of both the H/C method and other feasible parallel methods could benefit from reference standards, coordination and the use of best practice when conducting new assessments, as described by Leng et al. (2019) and discussed in section 4.1.4.

The evaluation of carbon sequestration potential in biochar is just a part of the climate mitigation potential. The system perspective includes the complex context of effects on the surrounding environment, effect on prevailing energy and waste management system. The current state of knowledge and the fact that the effects on the climate are context dependent makes it difficult to estimate the actual climate effect as a result of the application. However, the direct carbon sequestration in the biochar is a quantifiable parameter and together with the stability of the sequestered carbon, highly important for the accounting of climate mitigation measures.

References

Literature:

- Andersson, S., 2018. *Marknaden för biokol i Sverige*. Rapport 2018:14. Avfall Svergies Utvecklingssatsning ISSN 1103-4092. Malmö: Avfall Sverige, 2050 Consulting.
- Andrade, C., Trugilho, P., Gherardi Hein, P., Lima, J. & Napoli, A., 2012. Near Infrared Spectroscopy for Estimating Eucalyptus Charcoal Properties. *Journal of Near Infrared Spectroscopy*, 20 (6), pp 657-666. <https://doi.org/10.1255/jnirs.1028>.
- Budai, A., Zimmerman, A.R., Cowie, A.L., Webber, J.B.W., Singh, B.P., Glaser, B., Masiello, C.A., Andersson, D., Shields, F., Lehmann, J., Camps Arbestain, M., Williams, M., Sohi, S. & Joseph, S., 2013. Biochar Carbon Stability Test Method: An Assessment of Methods to Determine Biochar Carbon Stability. Technical report. Available at: https://www.researchgate.net/publication/298722030_Biochar_Carbon_Stability_Test_Method_An_assessment_of_methods_to_determine_biochar_carbon_stability [Accessed 14 May 2019]
- Budai, A., Calucci, L., Rasse, D.P., Strand, L.T., Pengerud, A., Wiedemeier, D., Abiven, S. & Forte, C., 2017. Effects of pyrolysis conditions on Miscanthus and corncob chars: characterization by IR, solid state NMR and BPCA analysis. *Journal of Analytical Applied Pyrolysis*, 128, pp 335–345. <https://doi.org/10.1016/j.jaap.2017.09.017>.
- Calvelo Pereira, R., Kaal, J., Camps Arbestain, M., Pardo Lorenzo, R., Aitkenhead, W., Hedley, M., Macías, F., Hindmarsh, J. & Maciá-Agulló, J.A., 2011. Contribution to characterization of biochar to estimate the labile fraction of carbon. *Organic Geochemistry*, 42 (11), pp 1331–1342. <https://doi.org/10.1016/j.orggeochem.2011.09.002>.
- Conti, R., Fabbri, D., Vassura, I. & Ferroni, L., 2016. Comparison of chemical and physical indices of thermal stability of biochars from different biomass by analytical pyrolysis and thermogravimetry. *Journal of Analytic and Applied Pyrolysis*, 122, pp 160–168. <https://doi.org/10.1016/j.jaap.2016.10.003>.
- Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P. & Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy*, 5 (2), pp 122–131. <https://doi.org/10.1111/gcbb.12030>.
- Cross, A. & Sohi, S.P., 2013. A method for screening the relative long-term stability of bio- char. *GCB Bioenergy*, 5 (2), pp 215–220. <https://doi.org/10.1111/gcbb.12035>.
- Cross, A. & Sohi, S.P., 2011. The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biology & Biochemistry*, 43(11), pp 2127-2134. <https://doi.org/10.1016/j.soilbio.2011.06.016>.
- Enders, A., Hanley, K., Whitman, T., Joseph, S. & Lehmann, J., 2012. Characterization of bio- chars to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* 114, pp 644–653. <https://doi.org/10.1016/j.biortech.2012.03.022>.
- Fang, Y., Singh, B. & Singh, B.P., 2015. Effect of temperature on biochar priming effects and its stability in soils. *Soil Biology and Biochemistry*, 80, pp 136–145. <https://doi.org/10.1016/j.soilbio.2014.10.006>.
- Gitau, K.J., Mutune, J., Sundberg, C., Mendum, R. & Njenga, M., 2019. Implications on Livelihoods and the Environment of Uptake of Gasifier Cook Stoves among Kenya's Rural Households. *Applied science*, 9(6), art nr.1205. <https://doi.org/10.3390/app9061205>.
- Gómez, N., Rosas, J.G., Singh, S., Ross, A.B., Sánchez, M.E. & Cara, J., 2016. Development of a gained stability index for describing biochar stability: relation of high recalcitrance index (R50) with accelerated ageing tests. *J. Anal. Appl. Pyrolysis* 120, pp 37–44. <https://doi.org/10.1016/j.jaap.2016.04.007>.
- Harvey, O.R., Kuo, L., Zimmerman, A.R., Louchouart, P., Amonette, J.E. & Herbert, B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). *Environ. Sci. Technol.* 46, pp 1415–1421. <https://doi.org/10.1021/es2040398>.
- Hemlin, H. & Lalangas, N., 2018 Production of Biochar Through Slow Pyrolysis of Biomass: Peat, Straw, Horse Manure and Sewage Sludge. Degree project in Engineering Chemistry. 2019 at KTH, Royal Institute of Technology.
- IPCC, 2018: de Coninck, H., A. Revi, M. Babiker, P. Bertoldi, M. Buckeridge, A. Cartwright, W. Dong, J. Ford, S. Fuss, J.-C. Hourcade, D. Ley, R. Mechler, P. Newman, A. Revokatova, S. Schultz, L. Steg, and T. Sugiyama, 2018: Strengthening and Implementing the Global Response. In: *Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty* [Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (eds.)]. <https://www.ipcc.ch/sr15/>
- Jeong, K., Choi, D., Lee, D., Kim, J., Kim, H., Ok, S. & Kwon, E., 2018. CO₂-looping in pyrolysis of horse manure using CaCO₃. *Journal of Cleaner production*, 174, pp 616-624. <https://doi.org/10.1016/j.jclepro.2017.11.022>.
- Kaal, J., Schneider, M.P.W., & Schmidt, M.W.I., 2012. Rapid molecular screening of black carbon (biochar) thermosequences obtained from chestnut wood and rice straw: a pyrolysis-GC/MS study. *Biomass Bioenergy* 45, pp 115–129. <https://doi.org/10.1016/j.biombioe.2012.05.021>.

- Kammann, C., Schmidt, H.P., Messersmidt, N., Linsel, S., Steffens, D., Muller, C., Koyro, H.W., Conte, P. & Joseph, S., 2015. Plant growth improvement mediated by nitrate capture in co-composted biochar. *Nature scientific reports*. DOI: 10.1038/srep11080
- Kuzyakov, Y., Bogomolova, I. & Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific ^{14}C analysis. *Soil Biol. Biochem.* 70, pp 229–236. <https://doi.org/10.1016/j.soilbio.2013.12.021>.
- Larenc, K. & Lal, R., 2014. Biochar application to soil for climate change mitigation by soil organic carbon sequestration. *Journal of Plant Nutrition and Soil Science*. 177(5). <https://doi.org/10.1002/jpln.201400058>
- Lehmann, J., Gaunt, J. & Rondon, M., 2006. Biochar Sequestration in Terrestrial Ecosystems – a Review. *Mitigation and Adaptation Strategies for Global Change*. 11(2), pp 401–427. <https://doi.org/10.1007/s11027-005-9006-5>
- Lehmann, J. & Joseph, S. (Eds.), 2009. *Biochar for Environmental Management: Science, Technology and Implementation*. Derby: Routledge.
- Lehmann, J., Joseph, S. (Eds.), 2015. *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed. Routledge, London and New York. <https://doi.org/10.4324/9781849770552>.
- Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2018. Biochar stability assessment methods: a review. *Science of the Total Environment*. 647, 210–222. <https://doi.org/10.1016/j.scitotenv.2018.07.402>.
- Leng, L., Xu, X., Wei, L., Fan, L., Huang, H., Li, J., Lu, Q., Li, J. & Zhou, W., 2019. Biochar stability assessment by incubation and modelling: Methods, drawbacks and recommendations. *Science of the Total Environment*. 664, pp 11–23. <https://doi.org/10.1016/j.scitotenv.2019.01.298>.
- Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J.E., Skjemstad, J.O., Luizão, F.J., Engelhard, M.H., Neves, E.G. & Wirick, S., 2008. Stability of biomass-derived black carbon in soils. *Geochimica et Cosmochimica Acta*. 72(24), 6069–6078. <https://doi.org/10.1016/j.gca.2008.09.028>.
- Linné, C.V. 1734. *Dalaresan- tillsammans med bergslagsresan*. A collaboration with Högskolan Dalarna, Dalarnas museum and Gullers bokförlag. Printed in Italy 2007. ISBN: 978-91-88238-65-8
- Liu, H., 2011. Small and Micro Combined Heat and Power (CHP) Systems, Advanced Design, Performance, *Materials and Applications Woodhead Publishing Series in Energy*. pp 88–122. <https://doi.org/10.1533/9780857092755.1.88>.
- Lyngfelt, A., Johansson, J.A. & Lindeberg, E., 2018. Negative CO₂ Emissions - An Analysis of the Retention Times Required with Respect to Possible Carbon Leakage. 14th Greenhouse Gas Control Technologies Conference Melbourne 21–26 October 2018 (GHGT-14). Available at SSRN: <https://ssrn.com/abstract=3366366>
- McBeath, A.V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I. & Plant, E.L., 2011. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. *Organic Geochemistry*. 42(10), pp 1194–1202. <https://doi.org/10.1016/j.orggeochem.2011.08.008>.
- Manyà, J.J., Ortigosa, M.A., Laguarda, S. & Manso, J.A., 2014. Experimental study on the effect of pyrolysis pressure, peak temperature, and particle size on the potential stability of vine shoots-derived biochar. *Fuel* 133, pp 163–172. <https://doi.org/10.1016/j.fuel.2014.05.019>.
- Mašek, O., Brownsort, P., Cross, A. & Sohi, S., 2013. Influence of production conditions on the yield and environmental stability of biochar. *Fuel* 103, pp 151–155. <https://doi.org/10.1016/j.fuel.2011.08.044>.
- Nguyen et al 2010. Temperature Sensitivity of Black Carbon Decomposition and Oxidation
Influence of production conditions on the yield and environmental stability of biochar
- Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S. & Masiello, C.A., 2010. Temperature sensitivity of black carbon decomposition and oxidation. *Environ. Sci. Technol.* 44(9), pp 3324–3331. <https://doi.org/10.1021/es903016y>.
- Qambrani, N. A., Rahman, M. M., Won, S., Shim, S., & Ra, C., 2017. Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review. *Renewable and Sustainable Energy Reviews*, 79, pp 255– 273. <https://doi.org/10.1016/j.rser.2017.05.057>
- Rombolà, A.G., Fabbri, D., Meredith, W., Snape, C.E. & Dieguez-Alonso, A., 2016. Molecular characterization of the thermally labile fraction of biochar by hydropyrolysis and pyrolysis-GC/MS. *J. Anal. Appl. Pyrolysis* 121, pp 230–239. <https://doi.org/10.1016/j.jaap.2016.08.003>.
- Shackley, S., Ruysschaert, G., Glaser, B. & Zwart, K., 2016. *Biochar in European Soils and Agriculture, Science and Practice*. New York: Routledge.
- Singh, B.P., Cowie, A.L. & Smernik, R.J., 2012. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. *Environmental Science & Technology*. 46(21), pp 11770–11778. <https://doi.org/10.1021/es302545b>.
- Singh, B., Fang, Y., Cowie, B.C.C. & Thomsen, L., 2014. NEXAFS and XPS characterisation of carbon functional groups of fresh and aged biochars. *Org. Geochem.* 77, pp 1–10. <https://doi.org/10.1016/j.orggeochem.2014.09.006>.
- Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Management*. 1, pp 289–303. <https://doi.org/10.4155/cmt.10.32>.
- Suárez-Abelenda, M., Kaal, J. & McBeath, A.V., 2017. Translating analytical pyrolysis fingerprints to Thermal Stability Indices (TSI) to improve biochar characterization by pyrolysis-GC-MS. *Biomass Bioenergy*. 98, pp 306–320. <https://doi.org/10.1016/j.biombioe.2017.01.021>.

- Söderqvist, H., 2017. Biochar for the City and the Earth – Fuel use in a new biochar plant. Industrial Ecology. Bachelor thesis at KTH, Royal Institute of Technology.
- Wang, J., Xiong, Z. & Kuzyakov, Y., 2016. Biochar stability in soil: meta-analysis of decomposition and priming effects. *GCB Bioenergy*. 8(3), pp 512–523. <https://doi.org/10.1111/gcbb.12266>.
- Weber, K. & Quicker, P., 2018. Properties of biochar. *Fuel*. 217, pp 240–261. <https://doi.org/10.1016/j.fuel.2017.12.054>.
- Wiedemeier, D.B., Abiven, S., Hockaday, W.C., Keiluweit, M., Kleber, M., Masiello, C.A., McBeath, A.V., Nico, P.S., Pyle, L.A., Schneider, M.P.W., Smernik, R.J., Wiesenberger, G.L.B. & Schmidt, M.W.I., 2015a. Aromaticity and degree of aromatic condensation of char. *Organic Geochemistry*. 78, pp 135–143. <https://doi.org/10.1016/j.orggeochem.2014.10.002>.
- Wiedemeier, D.B., Brodowski, S. & Wiesenberger, G.L.B., 2015b. Pyrogenic molecular markers: linking PAH with BPCA analysis. *Chemosphere*. 119, pp 432–437. <https://doi.org/10.1016/j.chemosphere.2014.06.046>.
- Willard, H.H., Merritt, L.L., Dean, J.A. & Settle, F.A., 1988. Instrumental Methods of Analysis. Seventh edition. Wadsworth Publishing Company, Belmont, California.
- Woolf, D., Amonette, J.E., Street-Perrott, A., Lehmann, J. & Joseph, S., 2009. Sustainable biochar to mitigate global climate change. *Nature Communications*. 1(56). DOI: 10.1038/ncomms1053.
- Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environmental Science & Technology*. 44(4), pp 1295–1301. <https://doi.org/10.1021/es903140c>.
- Zimmerman, A.R., Gao, B. & Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*. 43(6), pp 1169–1179. <https://doi.org/10.1016/j.soilbio.2011.02.005>.
- Zimmerman, A.R. & Gao, B. (2013). The Stability of Biochar in the Environment. In: Biochar and Soil Biota, (N. Ladygina and F. Rineau, eds.), CRC Press, Boca Raton, FL.

Communication and online:

- Dahlén, E., 2019. Research & Development Manager at Stockholm Exergi. (Personal Communication February 2019).
- EBC, 2012. 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.european-biochar.org/en/download>. Version 8.2E of 19th April 2019, DOI: 10.13140/RG.2.1.4658.7043
- Eurofins 2019. Prislita Bränslen och askor. [pdf] Available at: <https://cdnmedia.eurofins.com/european-east/media/2849814/prislita-braensle-2019.pdf> [Accessed 14 May 2019]
- Gustavsson, K., 2019. Industrial doctorate candidate in Industrial Ecology at KTH and Strategic development manager at Stockholm Exergi (Personal Communication January - May 2019).
- IBI, 2018. International Biochar Initiative. *Property Classifications in the IBI Biochar Classification Tool* [online] Available at: <https://biochar-international.org/biochar-classification-tool/>. [Accessed 14 May 2019]
- Smith, H.P., 2019. IBI Webinarium. *Pyrogenic Carbon Capture & Storage: a key climate technology*, presented by Hans-Peter Schmidt and moderated by Kathleen Draper
Broadcasted 20 February 2019. Available (Full slide set) to IBI members at: <https://biochar-international.org/members-only-home/>.
- Sundberg, C., 2019. Associate Professor in Industrial Ecology and Environmental Management. Department of Sustainable Development, Environmental Science and Engineering (SEED) KTH. (Personal Communication February 2019).
- SVOA, 2019. Stockholm Vatten och Avfall. *Biokol – för ett grönare Stockholm*. [online] Available at: <http://www.stockholmvattenochavfall.se/aktuellt/utvecklingsprojekt/biokol2/> [Accessed 14 May 2019]
- Westin, J., 2019. Advisor statistics at Avfall Sverige. Discussion of the amount of soil/garden waste in the municipal solid waste fraction. [E-mail] (Personal communication mars 2019).
- Wibom, J., 2019. Business development at Ragnsell. Discussion on fate of soil and demolition waste [E-mail and phone] (Personal communication mars - may 2019).
- Zimmermann, A., 2019. Andrew R. Zimmerman, Ph.D. Department of Geological Sciences, University of Florida. Discussion of the data behind the H/C model presented in Budai et al., 2013. [E-mail] (Personal communication mars 2019).

Appendix: 1

Test of the H/C method with biochar data with known MRT and H/C.

Lehmann & Joseph (2015) assembled 111 different biochar and their estimated stability from 38 different studies and their MRT. In 8 of the 38 studies was there enough published elemental data on the specific biochar to connect a H/C ratio to the modeled MRT. This led to 15 individual data points to plot in the H/C model. The estimated MRT was recalculated to BC_{+100} according to: $BC_{+100} = BC e^{-k \cdot 100}$ where $MRT = 1/k$

REF	link	H/C ?	Feedstock	MRT	incubation time (year)	H/C	BC ₊₁₀₀ (from MRT)	model
Bruun et al., 2012	https://doi.org/10.1016/j.soilbio.2011.11.019	yes	Wheat straw FP525°C, SP(2h)525°C	6, 12	0,18	0,06, 0,02	0,0%, 0,0%	single
Cross and Sohi, 2011	https://doi.org/10.1016/j.soilbio.2011.06.016	no						
Kimetu and Lehmann, 2012	https://pdfs.semanticscholar.org/e408/193d4e5d5e37f5fe85817f1a7f675b846184.pdf	no						
Hilscher and Knicker, 2011	https://doi.org/10.1016/j.orggeochem.2010.10.005	no						
Bamminger et al., 2014	https://doi.org/10.1111/ejss.12074	no						
Zimmermann. A et al., 2011	https://doi.org/10.1016/j.soilbio.2011.02.005	no						
Hamer et al., 2004	https://doi.org/10.1016/j.orggeochem.2004.03.003	yes	Corn straw, Rye straw, Oak wood, SP(2h)350°C	38, 41, 113	0,16	0,61, 0,56, 0,52	7,2%, 8,7%, 41,3%	single
Hilscher et al., 2009	https://doi.org/10.1016/j.orggeochem.2008.12.004	no						
Bai et al., 2013	https://doi.org/10.1007/s11104-013-1745-6	no						
Stewart et al., 2013	https://doi.org/10.1111/gcbb.12001	yes	Oak wood pellets , FP(550°C)	51, 557	1,92	0.015	14,0% 83,6%	single
Luo et al., 2011	https://doi.org/10.1016/j.soilbio.2011.07.020	no						
Maestrini et al., 2014a	https://doi.org/10.1016/j.soilbio.2013.11.013	no						
Farrell et al., 2013	https://doi.org/10.1016/j.scitotenv.2013.03.090	no						
Keith et al., 2011	https://pubs.acs.org/doi/10.1021/es202186j	no						
Knicker et al., 2013	https://doi.org/10.1016/j.soilbio.2012.02.021	no						
Brid et al., 1999	https://doi.org/10.1029/1999GB900067	no						
Zimmermann. M et al., 2012	https://doi.org/10.1111/j.1365-2486.2012.02796.x	yes	acasia (natural fier)	133	0,5	0.35 0.22	Not possible to track MTR from the article to a specific value of the H/C ratio	
Nguyen et al., 2008	https://link.springer.com/article/10.1007/s10533-008-9220-9	no						
Maestrini et al., 2014b	https://www.biogeosciences.net/11/5199/2014/bg-11-5199-2014.pdf	yes	Pine sapplings, SP(5h)450°C	146	0,83	0,1058	50,40%	single
Singh.B.P et al., 2012	https://pubs.acs.org/focus.lib.kth.se/doi/10.1021/es302545b	no						
Cheng et al., 2008	https://doi.org/10.1029/2007JG000642	no						
Zimmermann. A, 2010	https://pubs.acs.org/doi/abs/10.1021/es903140c	no						
Calvelo Pereira et al., 2014	https://doi.org/10.1111/ejss.12096	yes	Acient archiological charcoal, forest tree dated 681y, 770y	183, 220	0,3	0,43, 0,52	57.9%, 63,5%	double
Singh.N et al., 2014	https://doi.org/10.1111/gcb.12459	no						
Spokas et al., 2009	https://pubag.nal.usda.gov/download/47667/PDF	yes	Mixed wood	212	0,27		Not possible to track MTR from the article to a specific value of the H/C ratio	
Zimmermann and Gao, 2013	<i>Biochar and soil biota</i>	no						
Bruun et al., 2013	https://doi.org/10.1111/ejss.12073	no						
Bruun et al., 2008	https://doi.org/10.1016/j.orggeochem.2008.04.020	no						
Hammes et al., 2008	https://doi.org/10.5194/bg-5-1339-2008	no						
Herath et al., 2014	https://onlinelibrary.wiley.com/doi/pdf/10.1111/gcbb.12183	yes	Corn stover, SP 350°C,550°C	311, 244	1,4	0,68, 0,47	72.5% 66,8%	trip
Kuzyakov et al., 2009	https://doi.org/10.1016/j.soilbio.2008.10.016	no						
Fang et al., 2014	https://doi.org/10.1111/ejss.12094	no						

Lehndorff et al., 2014	https://doi.org/focus.lib.kth.se/10.1111/gcb.12468	no						
Santos et al., 2012	https://doi.org/10.1016/j.soilbio.2012.04.005	yes	Pine wood, SP(5h)450°C Granitic /Andesitic soil	594, 902	0,49	0,52	84.5% 89.5%	double
Vasilyeva et al., 2011	https://doi.org/10.1016/j.soilbio.2011.05.015	no						
Major et al., 2010	https://doi.org/10.1111/j.1365-2486.2009.02044.x	yes	Mango wood, SP(48h)400-600°C	1314	2	0,022	92.7%	double
Liang et al., 2008	https://doi.org/10.1016/j.gca.2008.09.028	no						
Lehmann et al., 2008	https://www.nature.com/articles/ngeo358	no						
Novak et al., 2010	https://doi.org/focus.lib.kth.se/10.1016/j.geoderma.2009.10.014	no						

Values used in figure 5a		Values used in figure 5b	
H/C	BC100	H/C	BC100
0,2	0	0,43	57,9
0,06	0	0,52	63,5
0,61	7,2	0,68	72,5
0,56	8,7	0,47	66,8
0,52	41,3	0,49	84,5
0,015	14	0,49	89,5
0,015	83,6	0,022	92,7
0,1058	50,4		
0,43	57,9		
0,52	63,5		
0,68	72,5		
0,47	66,8		
0,49	84,5		
0,49	89,5		
0,022	92,7		

Two plots were made: one that included all the 15 data points regardless of what model that had been used to model the MRT. The other plot only uses the values that origin from the more accurate 2-pool (or more) model.

Appendix: 2 Carbon sequestration potential for the biochar project of Stockholm Exergi

Information of the process feedstock and estimated yield per year: (information from Stockholm Exergi)	
Feedstock garden waste	20 000 ton
Feedstock horse manure	5 000 ton
Yield of biochar	5 000 ton
Yield of heat	40 GWh
Availability	8 000 h

The distribution of origin of biochar is assuming to corresponds to the distribution of feedstock, meaning that 4000 ton biochar comes from garden waste and 1 000 ton derives from horse manure. Further is the given masses assumed to refer to dry mater.

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